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GENERAL EDITORS

R. H. FOWLER AND P. KAPITZA





THE  
SEPARATION OF  
GASES

BY  
M. RUHEMANN

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## PREFACE

MORE than forty years have elapsed since Carl von Linde first liquefied air on a commercial scale and so paved the way for fractionating gaseous mixtures. His was not an isolated invention. It was conceived eighteen years after air had, for the first time, been liquefied in the laboratory by Cailletet in Paris and Pictet in Geneva, after the thermal data of liquefied gases had been determined by Olszewski in Crakow. It was followed immediately by Dewar's work on hydrogen liquefaction in London and by the setting up at Leiden in Holland of Kamerlingh Onnes's famous low-temperature laboratory. It was, in fact, the natural outcome of the work of two scientific generations from Faraday to Lord Kelvin, and it was urgently demanded by the industrial developments of the nineteenth century. It has led to the establishment of a whole series of thriving industries and on it has been erected the intricate fabric of Low-Temperature Physics.

In the course of these last forty years, scientists and engineers in many countries have pooled their knowledge and experience and are gradually establishing low-temperature gas separation as a field of applied science. The first country to give this field official standing was the Soviet Union. There 'deep refrigeration', as it is called, is taught in universities and technical colleges. Recently two valuable text-books on the subject have appeared in Russian, one by Professor Gersh in Moscow and one by Professor Pavlov in Leningrad.

I am convinced that it is high time that 'deep refrigeration', or whatever we may decide to call it, received adequate attention in this country, and with this in mind I have written the following book. In several chapters, especially Chapters VII and X, I have made considerable use of the material collected in the Russian text-books, and I am glad to take this opportunity of expressing my appreciation to their authors. But the present volume differs very materially from its Russian predecessors in that it is addressed not only, and not even primarily, to university or college students of this subject. For such students do not and cannot yet exist. Before there can be students there must be teachers; and by presenting, as far as possible, a comprehensive review of the scientific and industrial aspects of gas separation, I am hoping to interest some of those many persons who, like myself, are working in the borderland of physics, chemistry, and engineering. I trust that some of these, attracted by what I consider

a fascinating and important field of work, will study it for themselves and impart their knowledge to others.

I am profoundly grateful to Professor R. H. Fowler, F.R.S., the Editor of this series, for many valuable suggestions, and to Dr. E. A. Guggenheim for very helpful discussions on questions of thermodynamics.

My thanks are also due to the authors and editors of articles and journals from which figures have been reproduced or adapted. Full references to these are quoted in the text.

M. R.

*June, 1940*

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Figs. 105, 107, and 108 appear as separate plates facing pages 164, 165.

# INTRODUCTION

## THE PRINCIPLE OF THERMODYNAMIC EQUILIBRIUM

ALL natural gases and all primary gaseous products of industrial processes are complicated mixtures containing a large number of chemical components in the most diverse proportions. In order that they may be put to economic use, it is often necessary to alter their compositions considerably. In many cases it is even profitable to separate gaseous mixtures into their pure chemical components. The processes employed to bring about changes in the composition of gaseous mixtures, whether these changes lead to pure components or merely to products differing in composition from the original mixture, are known as gas separation.

Let us consider at first, for the sake of simplicity, a binary gaseous mixture which is to be separated into its pure components. We must conceive a continuous process such that an uninterrupted current of mixture enters the plant at one point and two currents of pure gas leave it at two other points. Somewhere in the interior of the apparatus the actual separation takes place, either in one step or in several steps, or else in an infinite number of infinitesimal changes of concentration.

For this to occur, the apparatus must contain certain surfaces on either side of which the mixture will have different concentrations. If separation is effected in one step, we shall need, in principle, two such surfaces; the mixture is introduced between them and on the outer side of each a pure gas is emitted. For separation in several steps we shall need more surfaces and, in the limiting case, an infinite number, across which infinitely small concentration heads will subsist. These surfaces cannot, of course, consist of impermeable walls, since interaction must occur between the substance on one side and that on the other. As we shall see, the surfaces need not contain any bodies apart from the mixtures that are being treated.

There are several kinds of surfaces across which differences of concentration may be brought about and maintained. But of these a certain group is much more important than the others, and this group alone will concern us here. The surfaces of this group are characterized by the fact that across them a certain finite concentration head automatically comes into being and maintains itself of its own accord for an unlimited period of time. These surfaces are the phase boundaries of a system in thermodynamic equilibrium.

According to the laws of thermodynamics, a system consisting of



several components in several phases is in equilibrium if the temperature, pressure, and chemical potential of each component are the same in every phase. Thermodynamics does not require that the concentrations of each component be the same in every phase. On the contrary, the chemical potentials of the several components will, in general, not be the same in the various phases unless the concentrations differ. Except at certain singular points, two phases containing more than one component, when in equilibrium with each other, will have different compositions. This is the fundamental physical law underlying all commercial methods of gas separation.

Now it is a well-known fact that a system in equilibrium can have but one gaseous phase, since all gases are completely miscible. On the other hand, in order that phase boundaries may exist, we must have at least two phases. Hence it follows that one of the phases concerned must be in a state other than gaseous. In order to separate a gaseous mixture by methods involving phase equilibrium, at least part of the gas must be transformed into a state of different aggregation. This may be attained in various ways:

1. *The gas may be partly liquefied.* This can be achieved only at temperatures below the critical. Since the critical temperatures of most gases are below room-temperature, this entails refrigeration. This leads us to the low-temperature method of gas separation, which is of by far the greatest importance and is the subject of this book.

2. *Part of the gas may be dissolved in a liquid solvent.* This is a very frequent method for removing impurities of low concentration. It should be noted that, as concerns thermodynamic equilibrium, it differs from the first only through the introduction of a fresh component.

3. *Part of the gas may be sorbed on a solid sorbent.* Here again we can achieve thermodynamic equilibrium between the free gas and the phase consisting of the sorbed gas and the sorbent. We have again merely introduced a new component, this time a solid.

4. *Part of the gas may be chemically bound to a solid or liquid substance or may undergo some chemical reaction associated with a change of phase.* As in this case the reacting part of the gaseous mixture usually undergoes permanent changes and thus ceases to exist as such, these 'chemical' methods are usually not included in the term gas separation. However, in principle, the laws of thermodynamic equilibrium are independent of whether chemical reactions do or do not occur in the system. This type should therefore be included in our list.

All the above-cited devices, however different they may appear at

first sight, are based on the same fundamental phenomenon: a separation into several phases in equilibrium involves coexisting mixtures of different composition on either side of surfaces, and thus brings about partial separation of the mixture. Since these concentration heads are independent of time, they can be made the basis of continuous processes.

One phase boundary will generally not lead to complete separation of the mixture but only to a slight change in composition. To separate a gas into its pure components, the process has to be repeated. This is the science of gas separation which we shall have occasion to describe in subsequent chapters.

A few examples may serve to illustrate these arguments.

If atmospheric air, which we may here consider as a binary mixture, containing 79 per cent. of nitrogen and 21 per cent. of oxygen, be cooled to a temperature of  $-193^{\circ}\text{C}$ . at atmospheric pressure, it will separate into a gas containing 87 per cent. of nitrogen and a liquid containing 63 per cent. of nitrogen. A partial separation of the mixture will thus be effected, but to produce pure oxygen and pure nitrogen this process must be frequently repeated.

If air containing carbon dioxide be allowed to bubble through water, a considerable quantity of carbon dioxide will be dissolved. If the water be continuously replaced, a stationary state will be reached in which the air leaving the water will be practically free from carbon dioxide, though it will, of course, be saturated with water vapour. The composition of the liquid phase will differ very strongly from that of the gas with which it is in equilibrium, the former containing much more water and much less air than the latter. In this way air may be partially freed from carbon dioxide and, if required, the carbon dioxide may be regained by heating the water.

If air containing traces of acetylene be passed through a filter of active charcoal a certain amount of air and acetylene will be adsorbed. However, since charcoal adsorbs acetylene much more eagerly than air, the ratio of acetylene to air in the adsorbed phase will be much greater than in the gas. If sufficient fresh charcoal is used, the air leaving the filter will be practically freed from acetylene. In this case, a continuous process cannot be realized since the charcoal, being a solid, cannot be made to flow through the apparatus but must be replenished or regenerated at intervals.

If a mixture of argon and oxygen be passed over heated sulphur, the sulphur will be oxidized and the oxygen thus removed from the mixture

until its partial pressure is equal to the dissociation pressure of sulphur dioxide, which is negligibly small. In this case a stable chemical compound is formed, which cannot easily be decomposed. Thus the oxygen may be considered to have vanished permanently from the system and the process is no longer to be regarded as simple gas separation.

The processes employed in industry for separating the various gaseous mixtures reviewed in Chapter I of this book are based primarily on liquefaction at low temperatures. The other methods of bringing about two-phase equilibrium play a subsidiary role, in that they are used to remove certain impurities, present in small quantities, either before the main separating process commences or after it has been completed. For this reason a knowledge of the vapour-liquid equilibrium of systems containing more than one component, which is treated theoretically and experimentally in Chapter II, is of paramount importance for the design and understanding of industrial separating plant. The plant itself, in which the actual separation is effected, in spite of all superficial diversities, is always essentially a combination of a few standard parts or units. These are described in Chapter III and their scope and purpose briefly summarized. Chapter IV contains the general theoretical equipment needed to describe what happens inside a fractionating plant and to calculate numerically the results to be expected under given conditions. Here it is shown how, once again, apparently abstract thermodynamic functions assume a very real and concrete meaning. Certain special theoretical problems that appear in particular cases are discussed later as they arise. In Chapter V refrigeration is treated in its relation to gas liquefaction and separation and the various methods of gas liquefaction are analysed.

The first gas to be separated on a large scale by low-temperature methods was atmospheric air. It is therefore natural that most of the theory and a great deal of the practical experience of gas separation was gained by studying this particular mixture. In Chapters VI—IX the various problems are discussed which have arisen in connexion with the separation of air into oxygen, nitrogen, and the rare gases, and the several solutions of these problems are examined.

With the production of commercial hydrogen from coke-oven gas, certain new questions arose, connected firstly with the complexity of the mixture and secondly with the very low boiling-point of hydrogen, which, at the temperatures subsisting in the plant, may be considered as a 'permanent gas'. These questions are discussed in Chapter X. Some fresh aspects become apparent in Chapter XI, in which the pro-

duction of methane from various sources is considered as well as the separation of helium from the methane and nitrogen of natural gas.

One of the most complicated problems of gas separation is the removal of certain valuable constituents from the mixtures known as cracker gases that occur as by-products of oil-refining. Though the methods used are the same as in other cases and are by now familiar to the reader, the plants themselves are rather involved. They are treated briefly in the last chapter, from which it is apparent that they are still largely empirical. Much scope is left for ingenuity and vision in the theoretical mastery of these complex mixtures.



# I

## GASES AND THEIR USE

THE raw materials from which all pure gases are obtained can best be divided into two groups, one of which consists of atmospheric air alone and the other contains all the other gaseous mixtures which will be treated in this book.

The composition of the Earth's atmosphere, which is very accurately constant in respect to time and place, is given in Table 1. The concentrations are in per cent. by volume.

TABLE 1. *Composition of Atmospheric Air*

N <sub>2</sub>	78.03	H <sub>2</sub>	$1 \times 10^{-2}$
O <sub>2</sub>	20.99	Ne	$1.5 \times 10^{-3}$
A	0.933	He	$5 \times 10^{-4}$
CO <sub>2</sub>	0.03	Kr	$1.1 \times 10^{-4}$
		X	$0.8 \times 10^{-5}$

Only the hydrogen and carbon dioxide contents vary slightly. It is apparent that, for most practical purposes, air may be considered as a binary mixture of nitrogen and oxygen, which together make up 99 per cent. of the whole. The influence of argon and the other rare gases on the production of pure oxygen and nitrogen and the methods evolved to extract these rare gases themselves and isolate them in a pure state will be discussed in Chapter IX.

All the other gaseous mixtures with which we shall have to deal may be classed as 'organic gases' from the fact that they are all the results of the transformation of organic matter. The innate similarity of all these gases has been largely lost to view as a result of the uneven development of science and engineering throughout the centuries. Too much stress has been laid on the distinction between natural and artificial gases, the former term being reserved for gases emitted 'voluntarily' at many places on the Earth's crust, and the latter for gases produced as a result of industrial processes. In fact the changes in matter produced by human endeavour tend rather naturally to be exaggerated.

The natural gases, such as marsh gas, earth gas, fire-damp, dry and wet oil gases, and casing-head gas, differ notably in composition from the 'artificial' coal and coke-oven gases. The natural gases contain more saturated hydrocarbons and less olefines, hydrogen, and carbon monoxide. But, though we have no intention of entering into geo-chemical speculations, we may assert that the processes giving rise to

each have probably much in common. The conditions of temperature and pressure in the interior of the Earth at certain periods will not have differed very much from those inside the various retorts and coke-ovens devised by human beings. The main difference between what we produce and what nature furnishes without our co-operation lies in the fact that the Earth has many millions of years at its disposal, whereas man is limited by the proverbial 'three score years and ten' and is intent on producing large quantities of gas in a small fraction of that period.

The organic gases may reasonably be subdivided into those produced from coal and those produced from, or more or less closely connected with, mineral oils. Of the former the best known are *coal gas* (or *town's gas*), *coke-oven gas*, and what is now called *low-temperature carbonization gas*, together with the various forms of *producer gas*, and the gases obtained by the *hydrogenation of coal and lignite* according to up-to-date methods. Of the latter we must mention *natural gas* (or *earth gas*), *casing-head gas*, and the similar mixtures obtained in 'topping' petroleum, together with *cracker gases* and those gained from oil hydrogenation. The fact that natural gases are often found in districts completely devoid of mineral oils shall not deter us from including them in this category.

Historically the first gas to be put to large-scale commercial use was coal gas, obtained by distilling coal in closed retorts in the absence of air, steam, or any other foreign agent. The town's gas industry developed so rapidly in the nineteenth century, especially in England, that it quickly assumed a dominant position, to such an extent that, in most people's minds, 'gas' is equivalent to the particular mixture supplied by the gas companies for cooking, heating, and lighting. At a time when the oil and coke industries are producing vast quantities of gaseous mixtures of widely differing compositions, it is still unusual to consider whether the particular mixture supplied to our homes is particularly suited to its purpose and whether it might not be better utilized otherwise, possibly not as fuel at all.

The composition of coal gas varies to a lesser degree according to the coal used and to a greater extent with the temperature of distillation. In former times, when coal was distilled at 700–800°C., the principal constituents were light hydrocarbons, methane, ethylene, and a certain amount of ethane, and it was these gases, together with small quantities of benzene vapour, that produced the characteristic luminosity of the gas flame. After the invention of the gas mantle, which made luminous

flames unnecessary, and of better refractory materials, the temperature in the retorts was gradually raised to 1,100–1,300° C., with the result that the percentage of hydrocarbons in the gas went down and that of hydrogen increased. In the following table some typical figures are given for the composition of coal gas produced at various temperatures.

TABLE 2. *Composition of Coal Gas produced at Various Temperatures*

Temperature (C.):	750–900°		995°	1,370°
Locality:	London cannel coal	Heidelberg bituminous coal	Derbyshire gas coal	
CH <sub>4</sub> . . .	41.99	42.40	32.9	32.6
C <sub>n</sub> H <sub>m</sub> . . .	10.81	7.27	3.8	3.5
H <sub>2</sub> . . .	35.94	44.00	48.6	56.4
CO . . .	10.07	5.73	5.6	7.5
CO <sub>2</sub> . . .	1.19	0.37	2.2	..
N <sub>2</sub> . . .	..	..	6.6	..

The products of coal distillation are gas, coke, tar, and ammonia, but the gas industry is primarily interested in the gas. On the other hand, a very similar process, carried out in the coke-oven, produces primarily metallurgical coke and, as a by-product, coke-oven gas. The composition of this gas differs only slightly from that of coal gas, as the figures of Table 3 demonstrate, in which typical results of analysis of coke-oven gas are given from different sources.

TABLE 3. *Composition of Coke-oven Gas*

	Durham	Lancs.	Yorks. and Derby	New York	Detroit	Germany
CH <sub>4</sub> . .	28.0	33.9	30.0	25.5	23.5	26.2
C <sub>n</sub> H <sub>m</sub> . .	3.2	3.7	2.9	2.7	4.8	3.6
H <sub>2</sub> . .	48.0	49.1	50.0	48.7	43.2	46.5
CO . .	6.5	6.4	7.2	10.4	14.0	6.3
CO <sub>2</sub> . .	2.5	2.5	2.1	4.7	3.4	4.2
N <sub>2</sub> . .	11.8	4.4	7.2	8.0	11.1	13.1

The similarity of the two gases is not surprising when we consider that the process occurring in the retort is practically identical with that in the coke-oven. In both the coal is heated to about the same temperature in a fire-clay chamber, but whereas the retort is a small narrow vessel holding some 12 cwt. of coal, the charge of a coke-oven is from 15 to 25 tons. The retort is fired with producer gas, while the coke-oven is generally heated with a portion of the gas it yields. Usually 6 to 12 retorts are fired together in a single furnace or 'setting', while coke-ovens are arranged in batteries of 25 to 30 units. These are



flat rectangular chambers, which may be 40–45 ft. long, 12–20 ft. high, and 14–20 in. wide. After periods of carbonization varying from 12 to 22 hours, the coke is forced out with a ram and quenched. From the point of view of gas-making, the chief advantage of retort distillation is that it is far more flexible than carbonization in coke-ovens.

Whereas the gas industry developed particularly rapidly in England, the coke industry, and with it the production of coke-oven gas, is more evenly distributed over the various countries. This is mainly due to the fact that it developed later, at a period when Britain had lost her monopoly position in industry. It is also connected with the fact that a greater variety of coals can be treated in coke-ovens than in retorts.

Low-temperature carbonization gas is a by-product of a new process for producing a soft and easily ignitable semi-coke for domestic use. It is essentially similar to the gas formerly obtained in retorts at low temperatures, but contains rather more methane. Table 4 shows some typical examples.

TABLE 4. *Composition of Low-temperature Gas produced according to Various Methods*

	(1)	(2)	(3)
CH <sub>4</sub> † . . .	39.6	48	67
C <sub>n</sub> H <sub>m</sub> ‡ . . .	4.3	13	6
H <sub>2</sub> . . .	37.2	27	12
CO . . .	6.1	7	5
CO <sub>2</sub> . . .	4.0	3	4
N <sub>2</sub> . . .	8.8	2	6

† Contains a little ethane.

‡ Ethylene and propylene.

At present this process is not carried out on a very large scale and the gas is therefore available in insufficient quantities to be of interest from our point of view.

As against the above-mentioned gases, *producer gas* and a number of similar mixtures are the products of processes for the complete gasification of coal and coke. Whereas a great part of the calorific value of coal is left in the coke after distillation, gasification transfers the whole of this calorific value to the gas, though not in a very concentrated form. The specific calorific value of the gas itself is not high, as it contains practically no hydrocarbons and is adulterated with varying amounts of nitrogen and carbon dioxide. This is due to the fact that the gases are produced by passing steam or air over hot coal and coke.

The best-known gases of this type are producer gas proper, Mond gas, and water gas. All these mixtures are produced in vast quantities and are relatively cheap. Their approximate compositions are given in Table 5.

TABLE 5. *Composition of Gases of the Producer Gas Type*

	<i>Producer gas</i>	<i>Mond gas</i>	<i>Water gas</i>
CH <sub>4</sub> . .	3	4	0.5
C <sub>n</sub> H <sub>m</sub> . .	0.2	0.3	..
H <sub>2</sub> . .	12	25	49
CO . .	28	12	42
CO <sub>2</sub> . .	3	16	5
N <sub>2</sub> . .	54	43	3

The hydrogenation of coal, or the synthetic oil industry, is being specially developed in Germany with the object of making the country independent of oil imports. Similar work is being taken up in other countries, including Britain. The gases produced are similar to those obtained in the cracking and hydrogenation of mineral oil and motor spirit.

If we now turn from coal to oil, we have first to mention what is usually termed *natural gas*. Vast quantities of this gas are emitted at numerous places, but only in the U.S.A. and Canada is even a fraction of the gas utilized. Natural gas occurs as casing-head gas in most working oil wells, where it is quite obviously to be considered as very light petrol. It also occurs, removed from actual oil wells, but generally in oil-bearing districts, accompanied by greater or lesser quantities of oil that may be extracted from it. Gases containing more than 1 gallon of oil per 1,000 cub. ft. are termed 'wet' gases. The rest are known as 'dry'. But apart from these, immense gas wells have been discovered, e.g. in the U.S.A., Poland, and the U.S.S.R., in districts far removed from any vestiges of oil. It is suggested by some that this gas has migrated from oil-bearing districts through porous strata. Others believe that it has been formed quite independently of oil by some other natural process and from some other raw material.

The chief component of most natural gas is methane. The methane concentration varies from about 40 to well over 99 per cent. The other constituents are nitrogen and higher paraffins, mainly the lightest such as ethane and propane. Some natural gases also contain notable quantities of helium, the helium content varying from the minutest trace up to as much as 2 per cent. Table 6 gives the compositions of some natural gases from various sources.

TABLE 6. *Composition of Natural Gases*

U.S.A.

	<i>Monroe, La.</i>	<i>Amarillo, Tex.</i>	<i>Columbus, Ohio</i>	<i>Ashland, Ky.</i>	<i>Hughston, Kans.</i>	<i>Ashley, Utah</i>
CH <sub>4</sub> . . .	94.7	72.94	80.4	75.0	68.86	99.42
C <sub>2</sub> H <sub>6</sub> . . .	2.8	18.96	18.1	24.0	17.51	..
CO <sub>2</sub> . . .	0.2	0.39	0.0	0.0	0.10	0.20
N <sub>2</sub> . . .	2.3	7.71	1.5	1.0	13.33	0.24

(Amer. Institute of Mining and Metallurgical Engineers, **94**, 398 (1931); **107**, 347 (1934).)

U.S.S.R.

CH <sub>4</sub> . . . .	99.8	99.6	97.8	89.8	82.1	77.5	57.6	40.5†
C <sub>2</sub> H <sub>6</sub> . . . .	..	..	..	..	2.1	2.0	16.8	..
C <sub>3</sub> H <sub>8</sub> . . . .	..	..	..	..	..	1.3	15.0	..
C <sub>4</sub> H <sub>10</sub> . . . .	..	..	..	..	..	..	10.2	..
Air or N <sub>2</sub> . . . .	..	..	2.0	8.7	9.7	1.0	..	59.5†

† Private information.

(The Science of Petroleum, ii, 1507.)

POLAND

CH <sub>4</sub> . . .	78.8	72.2
C <sub>2</sub> H <sub>6</sub> . . .	12.6	13.1
C <sub>3</sub> H <sub>8</sub> . . .	6.1	1.5
C <sub>4</sub> H <sub>10</sub> . . .	2.5	2.2
Air . . .	..	11.0
H <sub>2</sub> S . . .	..	..

(Private information.)

IRAN

CH <sub>4</sub> . . .	81	36
C <sub>2</sub> H <sub>6</sub> . . .	16	32
C <sub>3</sub> H <sub>8</sub> . . .	..	9
C <sub>4</sub> H <sub>10</sub> . . .	..	15
Air . . .	2	1
H <sub>2</sub> S . . .	1	7

(Private information.)

*Helium-bearing Natural Gases*

U.S.A.

	<i>Dexter, Kans.</i>	<i>Eureka, Kans.</i>	<i>Petrolia, Tex.</i>	<i>Pearson, Okla.</i>	<i>Augusta, Kans.</i>
CH <sub>4</sub> . . .	14.85	51.80	56.85	59.33	74.74
C <sub>2</sub> H <sub>6</sub> , etc. . .	..	..	10.33	0.00	12.92
CO <sub>2</sub> . . .	..	..	0.25	0.00	0.19
O <sub>2</sub> . . .	..	..	0.54	0.45	0.57
N <sub>2</sub> . . .	82.70	46.40	31.13	39.59	11.08
He . . .	1.84	1.50	0.90	0.63	0.50

(Handbuch der anorganischen Chemie, 1928, vol. iv, part 3, section 1, p. 44.)

CANADA

	<i>Hamilton, Ontario</i>	<i>Calgary, Alberta</i>	<i>Moncton, N.B.</i>
CH <sub>4</sub> . . .	80	87.6	80
C <sub>2</sub> H <sub>6</sub> , etc. . .	12	0.9	7.2
N <sub>2</sub> . . .	8	11.2	12.8
He . . .	0.34	0.33	0.064

(Handbuch der anorganischen Chemie, 1928, vol. iv, part 3, section 1, p. 48.)

In Canada and the U.S.A. large quantities of natural gas are used for domestic firing and lighting, though greater quantities are still running waste. Fifty-two Canadian towns are now supplied with 'natural town's gas'. In both these countries the consumption of natural gas is greater than that of coal gas.

The total world utilization of natural gas in 1937 was about  $2.6 \times 10^{12}$  cub. ft., of which  $2.5 \times 10^{12}$  cub. ft. fell to the United States. This is only a small fraction of the gas emitted annually from the Earth's surface.

Cracking is the process employed to produce valuable petroils from crude oil poor in light constituents. It consists in subjecting the crude oil simultaneously to high pressures and high temperatures. In the course of this process large quantities of gas are developed, which consist mainly of light hydrocarbons. The composition varies greatly, but is usually maintained roughly within the following limits.

TABLE 7. *Composition of Cracker Gas*

$\text{CH}_4$	.	.	.	.	.	25-45
$\text{C}_2\text{H}_4$	.	.	.	.	.	15-30
$\text{C}_2\text{H}_6$	.	.	.	.	.	6-12
$\text{C}_3\text{H}_8$	.	.	.	.	.	5-15
$\text{C}_3\text{H}_8$ and higher hydrocarbons	.	.	.	.	.	10-15
$\text{H}_2$	.	.	.	.	.	5-20

The total production of cracker gas in the U.S.A. in 1936 was approximately  $3 \times 10^{11}$  cub. ft. Very similar gases are evolved during the hydrogenation of oil and coal for the production of synthetic motor spirit.

Finally, one more type of organic gas should be mentioned, and that is *sewage gas*. In the course of the digesting process employed for the disposal of sewage, large quantities of gas are developed, consisting of 70 per cent. methane and 30 per cent. carbon dioxide. In up-to-date sewage works this gas is utilized as fuel. In the West Middlesex Main Drainage Works at Isleworth, 350 million cub. ft. of sewage gas are produced annually, of which 280 million are converted to power and utilized on the spot. Similar conditions exist in Birmingham and in several continental and American towns. The world production of sewage gas is increasing rapidly and the total output will soon be of the same order of magnitude as that of other better-known organic gases.

The foregoing review, though necessarily incomplete, will serve to convey some idea of the extent and nature of the manifold gases surrounding us. It will also show how uneven is the technical development in this sphere. Some gases, such as coal gas, have been known for over

a century and have a long tradition of usefulness in the minds of the public. Natural methane-bearing gases have been known to exist from time immemorial, but only in recent years have they begun to play a part in economic life. Cracker gases and the similar products of hydrogenation are comparatively recent achievements and are the result of the development of the motor-car industry with its rising demand for particular types of petrol. The all-pervading atmosphere is perhaps the most flagrant example of delayed development. For many millions of years we have done nothing but breathe it, and not till the last generation have we learned to weld with one of its components, produce fertilizers with a second, light our homes with the help of a third, and advertise our products with the glaring red light from a fourth.

In view of these facts it is not surprising that the utilization of gas, at the time of writing, is largely haphazard. Certain gases are used for certain purposes, not because these are the most rational ways of using them, but because they were or appeared to be rational fifty years ago, and since then so much capital has been invested in them that it was unprofitable to make any extensive changes.

The only gas that is now more or less rationally exploited is atmospheric air. Apart from numerous processes in which air is employed in an unchanged condition, such as the gasification of coal and the production of steel, air can be separated into oxygen and nitrogen and the various rare gases. For the last thirty-five years oxygen from the air has been used to an increasing extent for cutting, welding and similar purposes. Up to the last war, oxygen was the only constituent of air to be utilized on a commercial scale. In the early twenties, with the advent of synthetic fertilizers, increasing quantities of nitrogen were in demand. Now large amounts of nitrogen are combined with hydrogen to form ammonia, which is the basis of the fertilizer industry and also incidentally of the production of most important explosives. At about the same time it was found profitable to fill incandescent lamps with argon, as this gas, with its high atomic weight, prevents vaporization of the filaments and thus allows the lamps to be maintained at a higher temperature than when filled with nitrogen, with a corresponding economy in the cost of candle-power.

In recent years attempts have been made to replace argon with mixtures of krypton and xenon, whose atomic weights are still higher. The extraction of krypton and xenon from air is a difficult task, owing to their very low concentrations; but the problem has been solved

in principle and the commercial exploitation of these gases is now beginning.

Neon is now being used in considerable quantities in discharge tubes owing to the brilliant red light which it emits and which gives it great advertisement value. The blue light from argon is also useful in this connexion. Other possibilities of utilizing neon have been suggested, but have hitherto not been put into practice.

The extraction of helium from air is not a commercial proposition, since helium may be obtained more cheaply from natural gases.

From the point of view of some world-planning committee, seeking to employ all gases to the greatest advantage of the community, it would appear rational to distinguish the following three groups of constituents in organic gases:

1. Hydrogen and carbon monoxide.
  2. Paraffins.
  3. Olefines and other unsaturated hydrocarbons.
1. Hydrogen and carbon monoxide have comparatively low calorific values but valuable chemical properties. Their utilization as fuel would appear uneconomical in a very general sense. The most rational utilization of hydrogen should be for synthetic ammonia and hydrogenation, and carbon monoxide should, for the same reason, be used preferably for various chemical syntheses.
  2. The light paraffins that form constituents of gaseous mixtures are methane, ethane, propane, and butane. All have high calorific values and are chemically more or less inert. They should be used preferably as fuel and varied according to local conditions.
  3. Though ethylene, propylene, and butylene form excellent fuel, they are too valuable to be used as such, as they have very useful chemical properties. They should be utilized preferably in chemical industry.

Clearly these complex problems cannot be solved superficially in the way indicated. The suggestions set forth above are not to be considered as a solution but are rather intended to point out that the problems exist at all. They have purposely presupposed that all the constituents named can be extracted from the crude mixtures available and that any difficulties in the process of separation are to be neglected in discussing rational utilization. It is one of the objects of this book to show that this standpoint is justified. The problem of separating gases into more or less pure components is in fact solved, in the sense that

the fact of a certain constituent appearing in a mixture with other constituents is no longer an argument in favour of its being utilized together with these other constituents. This is a new and important fact which, it must be realized, is ushering in a new period of industrial development.

Let us now consider how organic gases are in fact being utilized. We have already stated that in the U.S.A. and Canada a small portion of the natural gas resources is being used for domestic and industrial heating. Since these gases consist largely of methane, this form of utilization may be considered as essentially rational. Considerable quantities of methane are also used for the manufacture of carbon black, which, with the present technique, is rather a wasteful process. It is evident that very much greater quantities of natural gas could be used to advantage as fuel, even in these countries. Elsewhere the vast natural gas wells are hardly utilized at all, with the possible exception of Poland. Iran and the U.S.S.R. are particularly rich in gas. In Iran, apparently, all the gas is wasted, and in the U.S.S.R. its utilization is only just beginning. In the latter country plans have been evolved to utilize methane for chemical purposes in connexion with the extraction of helium. In Canada and the U.S.A. no use has yet been made of the particularly excellent anti-knock properties of methane. Its use in internal-combustion engines has up to now been very slight and confined to Diesels. Methane could provide excellent fuel for high-power aero engines and for driving cars and lorries. It is used for the latter purpose to a certain extent in Germany, the gas being stored in high-pressure cylinders. It would probably be more profitable to store it as a liquid in tanks; it is so stored in the U.S.S.R. This question will be discussed in Chapter XI.

The extraction of helium from natural gases is carried out on an industrial scale in the U.S.A. and the U.S.S.R. The American sources are by far the richest in the world, and it is there considered uneconomical to work with a gas containing less than 0.5 per cent. He. The principal use to which helium is put is the filling of airships, since it is only twice as heavy as hydrogen and non-inflammable. The quantities needed for this purpose are so great that few countries have found it worth while to attempt to exploit their meagre resources. Helium is also used to dilute the oxygen in high-pressure diving bells, since compressed helium does not dissolve in the blood like nitrogen. Caisson disease is thus eliminated.

A much more complicated state of affairs is apparent when we con-

sider the utilization of the better-known organic gases, coal gas and coke-oven gas. As we have seen, the compositions of these two gases are almost identical and the quantities of each produced in the world are of the same order of magnitude of  $10^{12}$  cub. ft. per annum. But whereas coal gas is used almost exclusively for domestic lighting and heating, coke-oven gas has found a variety of applications. Part of this gas is used for the same purpose as coal gas, especially in Germany and in other countries with a large coke industry. Part is used in the coke factories and the metallurgical plants, when these are attached to them. A good deal is wasted, and in some countries, particularly Germany and the U.S.S.R., large quantities of coke-oven gas are separated to yield hydrogen for the synthetic ammonia and hydrogenation industries. The remaining constituents, loosely termed rich gas, are mostly used as fuel. The separation of coke-oven gas is one of the most highly developed processes of low-temperature industry and will concern us at some length in Chapter X.

The widely different uses to which coal gas and coke-oven gas are put are to be understood from the fact that coal gas is the primary product of retort distillation, which was, in fact, invented for the purpose of producing the gas, whereas coke-oven gas is a by-product of the coke industry. Gas light and gas fires in the middle of the last century represented a great advance on the former utilization of coal. At the time of writing, the utilization of a complicated mixture, containing components of very different thermal and chemical properties, for such simple purposes as lighting and heating appears rather anomalous, in view of the recent developments in the technique of gas separation and in chemical industry. But the vast sums of money invested in the gas industry make any changes in the utilization of gas costly and difficult, especially as all the gas made is also used and no spare gas is available.

Coke-oven gas, on the other hand, is largely free. Not much of it is wanted for the coke industry, and it is therefore available as a raw material for any new processes that enterprising people have seen fit to inaugurate.

The proper utilization of cracker gas and similar products is a new problem, just as these gases themselves are new. Most of it is still burned in spite of the valuable olefines that it contains. In America numerous patents exist for extracting the olefines, which are doubtless intended to be used for chemical synthesis. In Baku in the U.S.S.R. a large plant was recently started for the extraction of ethylene, pro-



pylene, and butadiene from cracker gas, and was apparently successful. The industries catered for are alcohol and artificial rubber. In other countries the instability of markets seems to be a strong deterrent to enterprise in this sphere, which should offer immense possibilities in the near future.

Synthetic gases in European countries and natural gases in Canada and the U.S.A. have yielded considerable quantities of propane and butane, which are useful for domestic heating and as motor fuel. Their advantage consists in the fact that they can be liquefied at room-temperature at fairly low pressures and are thus easy to store and transport. Their use as domestic fuel is largely confined to districts remote from industrial centres that have not yet been supplied with gas mains. Here 'bottle gas' (or 'calor gas'), as it is called, is a very welcome substitute. In Germany an increasing amount of this gas is being used to drive lorries and buses for reasons of self-sufficiency and economy in imported fuel.

## II

### THE EQUILIBRIUM OF GASEOUS AND LIQUID MIXTURES

#### 1. The equilibrium of binary mixtures

THE state of a homogeneous system, consisting of more than one component, is completely defined by temperature, pressure, and the mole fractions  $x_1, x_2, \dots, x_{n-1}$ , where  $n$  is the number of components in the system. The remaining mole fraction  $x_n$  is then given by the relation  $\sum_{i=1}^n x_i = 1$ . In the case of a binary system,  $p$ ,  $T$ , and  $x$  may be taken as independent variables, where  $x$  is the mole fraction of one of the two components. Every set of values  $p$ ,  $T$ , and  $x$  determines a state of the system, which thus has three degrees of freedom.

The presence of a second phase in equilibrium with the first reduces the number of degrees of freedom by one. Moreover, equilibrium can subsist only if the pressure and the temperature are the same in both phases. Therefore, of the four variables  $p$ ,  $T$ ,  $x_1$ ,  $x_2$ , where the subscripts refer to the two phases, only two are independent. If  $p$  and  $T$  are fixed, only one set of values  $(x_1, x_2)$  corresponds to a state in which the two phases are in equilibrium. Within certain limits, to each pair of values  $p$  and  $T$  there exists a definite pair of values  $x_1$  and  $x_2$ .  $x_1$  and  $x_2$  may both be considered as functions of  $p$  and  $T$ .

In a space with coordinates  $p$ ,  $T$ , and  $x$  we may therefore picture two surfaces, which we shall call *equilibrium surfaces*, one depicting the states of the first phase and the other those of the second phase. Each point on one surface will be related to a certain point on the other surface by the fact that two phases in states denoted by these points are in equilibrium with each other. Two such corresponding points are known as *nodes*, and straight lines joining a pair of nodes are called *connodals* or *tie-lines*. All connodals are by their nature perpendicular to the  $(p, T)$  coordinate plane. Therefore no two connodals can ever intersect.

In general two corresponding nodes will not coincide. For though thermodynamics requires that the pressure and temperature be the same in both phases, no such demand applies to concentrations. Indeed, as was stated in the introduction, the whole point in the use of phase equilibrium for gas separation is that in the two phases the concentrations differ.

The space between the two equilibrium surfaces is known as the *inhomogeneous region*. A point in this region does not define a stable

state of the system. When brought into a state represented by a point in the inhomogeneous region, the system will separate into two phases, represented by the two ends of the connodal through that point.

Thermodynamic analysis points to the existence of four types of curves on the equilibrium surfaces, which have a particular physical significance. These curves give a good idea of what to expect in a binary mixture.

Curves of the first type are called *pure component curves*. They mark the intersection of the equilibrium surfaces with the planes  $x = 0$  and  $x = 1$ . In these planes the mixture degenerates into a one-component system, in which  $x$  is either zero or unity in both phases. The pure component curves are simply the vapour-pressure curves of the two pure constituents.

Along certain curves on an equilibrium surface the tangential plane may be perpendicular to the  $(p, T)$  coordinate plane, so that  $(\partial p / \partial x)_T = (\partial T / \partial x)_p = 0$ . This may have one of two physical meanings. The two equilibrium surfaces may merge into each other along this curve and so become a single surface, like a loosely folded piece of paper;<sup>†</sup> or the two surfaces may touch along the curve, but nowhere else. In the first case the curve is known as a *critical curve*, in the second case it is termed a *curve of equal composition*.

These phenomena may be made clearer by considering sections parallel to the  $(p, x)$  or  $(T, x)$  planes. The equilibrium surfaces intersect these plane sections in curves, which are called *equilibrium curves*. In the neighbourhood of a point on the critical curve of the equilibrium surface, the  $(p, x)$  or  $(T, x)$  section has the form shown in Fig. 1. The critical point  $K$  is a point on the critical curve, which intersects the plane of the paper at this point. The two curves, representing sections of the equilibrium surface with the plane of the paper, merge into one at  $K$ . In this and in subsequent figures the shaded areas mark the inhomogeneous regions.

A  $(p, x)$  or  $(T, x)$  section near a curve of equal composition is shown in Fig. 2.  $L$  is a point on the curve of equal composition, which must again be considered as intersecting the plane of the paper at this point. In the case of Fig. 1 the critical nature of point  $K$  is immediately clear from the fact that we may pass freely around  $K$  from one phase to the other without traversing the inhomogeneous region. In the case of a point of equal composition, as shown in Fig. 2, this is not possible.

<sup>†</sup> The folded sheet of paper is an example of a surface which can be unfolded on to a plane. In general this will not be possible.

Finally, the system may pass into states in which a third phase makes its appearance. The effect of this is to remove another degree of freedom, so that these states must lie on one or more curves on the  $(p, T, x)$  surfaces. These *three-phase curves* may be considered as arising

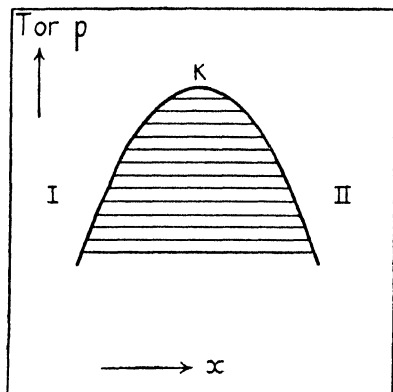


FIG. 1. Equilibrium curve in the vicinity of a critical point. I and II denote the two phases

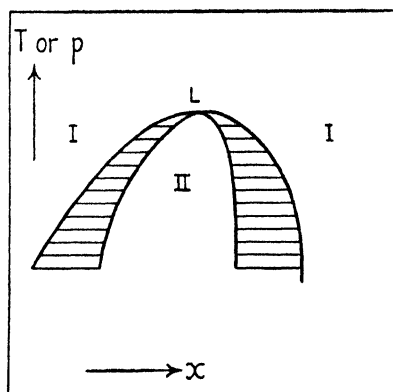


FIG. 2. Equilibrium curves in the vicinity of a point of equal composition

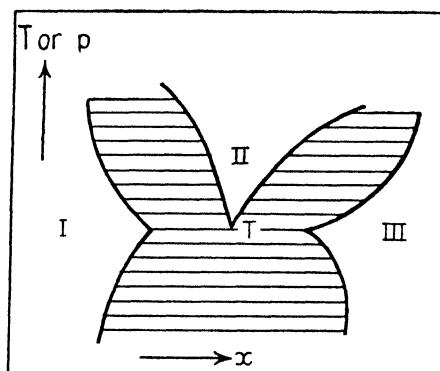


FIG. 3. Equilibrium curves in the vicinity of a triple point

in the following manner. Each pair of phases in equilibrium gives rise to two surfaces. For three phases we thus have six surfaces: two refer to equilibrium between phase I and phase II, two between phase II and phase III, and two between phase III and phase I. If all three phases are to be in equilibrium together, the six surfaces must intersect in pairs in such a manner that the three curves of intersection shall have the same values of  $p$  and  $T$  at all their points. Fig. 3 shows a section of the three pairs of surfaces parallel to the  $(p, x)$  or  $(T, x)$

plane. Of the three points of intersection in Fig. 3 the inner point  $T$  is known as the *triple point* and the locus of points  $T$  is called the three-phase curve.

We have discussed the typical forms of equilibrium diagrams in the neighbourhood of certain curves on the  $(p, T, x)$  surface. It is now

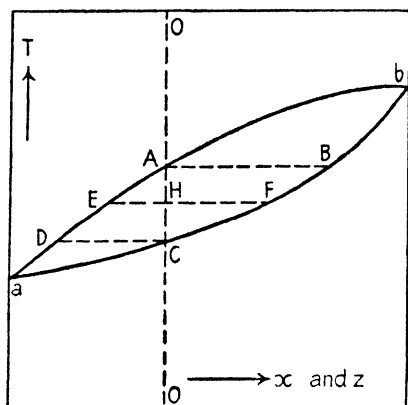


FIG. 4.  $(T, x)$  curves with pure component points  $a$  and  $b$ , showing process of condensation

easy to combine these results to show the typical forms that equilibrium curves may assume across the whole  $(p, x)$  or  $(T, x)$  planes. These curves will be familiar to most readers from their knowledge of solid-liquid equilibrium. We shall first consider sections of the surface parallel to the  $(T, x)$  plane, or, as they are usually termed,  $(T, x)$  diagrams.

When the liquid phases are miscible in all concentrations, as is the case with all systems that will concern us here, three types of  $(T, x)$  diagram may appear, as shown in Figs. 4, 5, and 6. In Fig. 4,  $a$  and  $b$  are pure component points, i.e. points on pure component curves on the corresponding  $(p, T, x)$  surface. Fig. 5 has a critical point at  $K$  and Fig. 6 a point of equal composition at  $L$ .  $K$  and  $L$  are points on the corresponding curves of the  $(p, T, x)$  surfaces. Thermodynamics shows that  $K$  and  $L$  are always either maxima or minima on the  $(p, x)$  and  $(T, x)$  diagrams. As a rule the  $(p, x)$  diagram is similar in shape to the  $(T, x)$  diagram, but it is always inverted as regards the  $x$ -axis. For if a change in composition leads to a rise in vapour pressure at constant temperature, the same change in composition, carried out at constant pressure, will lower the temperature at which the two phases are in equilibrium. The curve bounding the inhomogeneous region and the vapour phase is frequently called the *dew-curve*; that bounding the inhomogeneous region and the liquid phase is known as the *boiling-curve*.

If a binary system, having equilibrium curves as shown in Fig. 4, is cooled at constant pressure along the dotted line  $O-O$ , condensation commences at the dew-curve at the point  $A$  and the first drop of liquid condensed has the composition of point  $B$  on the boiling-curve. In order that condensation may proceed, the temperature must be lowered further. The composition of the liquid shifts to the left along the boiling-

curve and that of the vapour in the same direction along the dew-curve. Finally, when all the vapour has been liquefied, the liquid naturally has the same composition as the original gas (point *C*) and the last bubble of vapour is of the composition *D*.

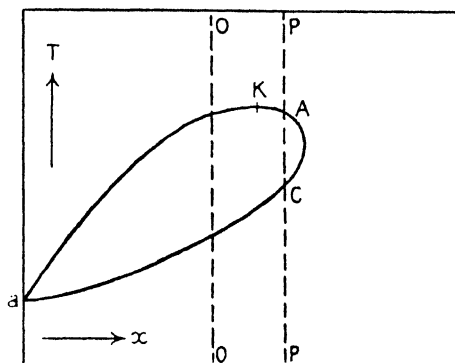


FIG. 5. ( $T, x$ ) curves showing critical point *K*

At a point *H* between *A* and *B*, in the inhomogeneous region, the ratio of the amount of vapour and the amount of liquid present may be determined as follows. The total mass present is the sum of the mass of the liquid and that of the vapour, and the same relation applies

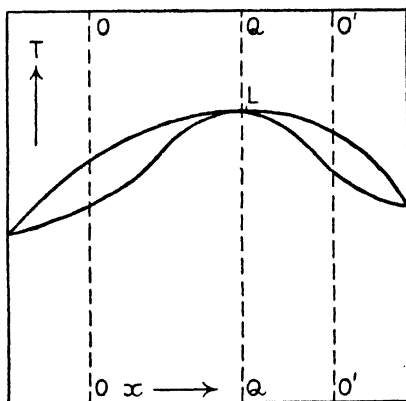


FIG. 6. ( $T, x$ ) curves showing point of equal composition *L*

to the mass of any one of the components. If  $M_x$ ,  $M_y$ , and  $M_z$  be the mass of the liquid phase, the mass of the original mixture, and the mass of the vapour phase respectively, and if  $x$ ,  $y$ , and  $z$  be the corresponding mole fractions of one of the two components,

$$M_y = M_x + M_z$$

D

and

$$M_y y = M_x x + M_z z;$$

whence

$$M_x/M_z = (z-y)/(y-x) = EH/HF.$$

This relationship is often called the *lever rule*. It is obviously applicable when  $M$  denotes any additive property and is not confined to the mass.

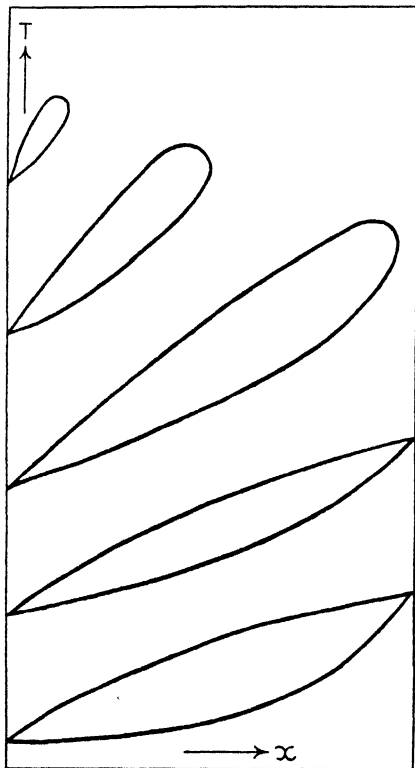


FIG. 7.  $(T, x)$  curves at various pressures above and below the critical point of one component

The same rule will be applied frequently later when the specific enthalpy  $h$  is taken as the ordinate instead of the temperature  $T$ . We see in Fig. 4 that, as the temperature falls from  $A$  to  $C$ , the ratio  $M_x/M_z = EH/HF$  increases from 0 to  $\infty$ . The amount of liquid gradually increases and the vapour vanishes.

The same phenomena occur if we cool the mixture along the dotted line  $O-O$  in Fig. 5 or along  $O-O$  and  $O'-O'$  in Fig. 6. However, things are different along the line  $P-P$ , situated to the right of the critical point  $K$  in Fig. 5. On cooling our mixture to point  $A$  the new phase formed is not a liquid but a gas. At any rate, it will appear at the top of the cooled vessel and not at the bottom, and we may conclude that the mixture we have been cooling was in fact not a gas but a liquid. On further cooling, this new vapour phase will at first increase in mass

and then again decrease. At point  $C$  it will finally vanish altogether and only a liquid phase will remain. This phenomenon, which is called *retrograde condensation*, was discovered by Kuenen. It appears natural enough when we realize that, in a closed vessel, there is no way of distinguishing between a gas and a liquid as long as only one phase is present. It appears strange to us at first because we are used to liquids with free surfaces, i.e. bounded by air or vapour.

With the  $(T, x)$  curves of Fig. 5, and similarly with  $(p, x)$  curves, we cannot prove that the new phase formed is a vapour and not a

liquid. The phenomenon becomes strikingly clear when we employ a  $(v, x)$  diagram, in which  $v$  is the specific volume. The  $(v, x)$  curves show at once that the new phase has a greater volume than the original mixture, i.e. a smaller density. However, we have refrained from introducing  $(v, x)$  diagrams as they are seldom used and might disconcert the reader.

On cooling a mixture along the line  $Q-Q$  through the point of equal composition  $L$  on Fig. 6, complete condensation occurs at constant temperature as in the case of a pure substance. This is the principal characteristic of points of equal composition.

Fig. 5 may be considered as having developed from Fig. 4 with rising pressure. Consider a series of  $(T, x)$  curves at various pressures (Fig. 7). As the pressure is raised the curves gradually move upwards, since the boiling-point of a substance is raised when the pressure increases. Finally, the critical point of one of the components may be reached. The  $(T, x)$  curves above this pressure will break away from the ordinate axis corresponding to this component and, when the pressure is raised further, recede across the figure and finally vanish at the critical point of the other component.

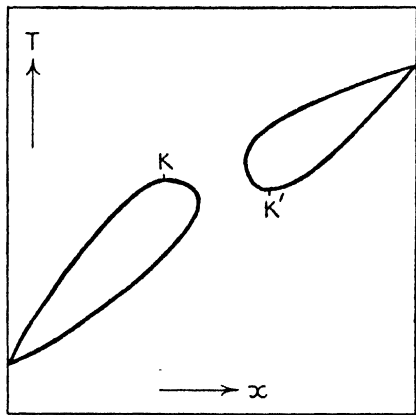


FIG. 8.  $(T, x)$  curves with two critical points

Occasionally it may happen that the critical curve of the mixture begins below the critical point of either component. In this case the  $(T, x)$  curves break asunder in the middle of the diagram, as shown in Fig. 8. The phenomena of retrograde condensation occurring in this case may be inferred from the figure.

The following arguments, though they might be illustrated quite well on the  $(T, x)$  diagram, will appear more familiar in  $(p, x)$  coordinates. Consider a  $(p, x)$  diagram with a critical point, as shown at the top of Fig. 9. Suppose the critical point to be a maximum on the  $(p, x)$  curve. As the temperature is reduced the inhomogeneous region will move downwards, and we should expect it to spread across the diagram and finally lead to a pure component point, as in the  $(T, x)$  diagram of Fig. 7. In many cases this actually occurs, but occasionally the phenomena are different. The inhomogeneous region may spread out in all



directions, as shown in Fig. 10, and finally the critical point may recede to indefinitely high pressures. In fact it will eventually reach the solidification curve. This type of equilibrium curve will frequently

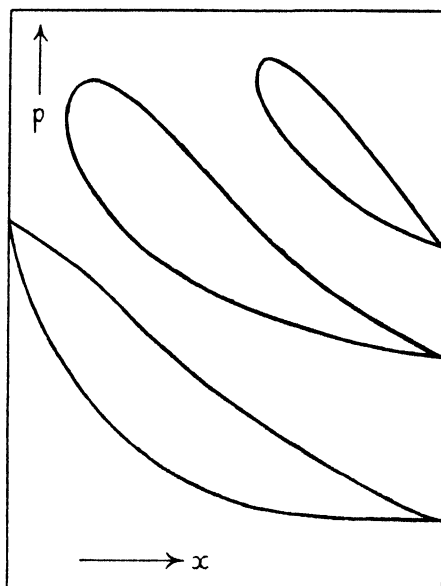


FIG. 9.  $(p, x)$  curves at various temperatures when critical points of components are close together

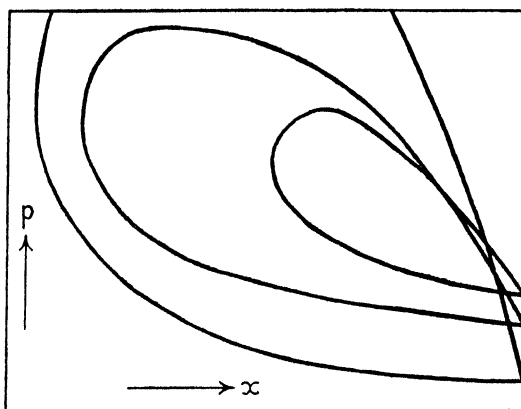


FIG. 10.  $(p, x)$  curves at various temperatures when critical points of components are far apart

occur in subsequent sections and is characteristic of a mixture in which the critical points of the two components are far apart.

We have here discussed merely three types of curves on the  $(p, T, x)$  surface. The fourth type, i.e. the three-phase curves, will not concern

us in future, so it will suffice to give the essential features in the  $(T, x)$  form in Figs. 11 and 12.

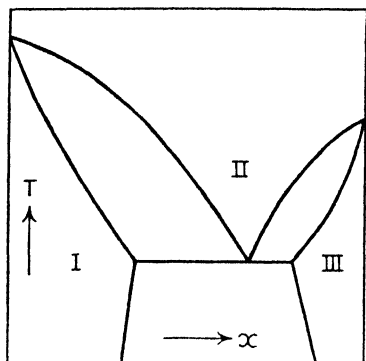


FIG. 11.  $(T, x)$  curves with triple point. Phase II exists above three-phase curve only

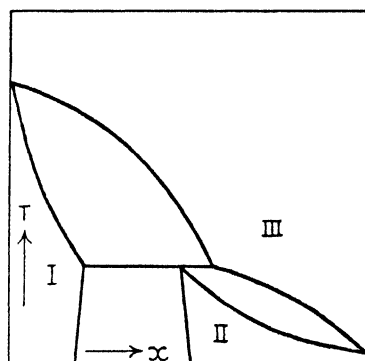


FIG. 12.  $(T, x)$  curves with triple point. Phase II exists below three-phase curve only

## 2. Ternary mixtures

A system of three components in two-phase equilibrium, as is clear from the beginning of the last section, has three degrees of freedom. The variables of the system, apart from temperature and pressure, are the two concentrations  $x_1$  and  $x_2$  of the components 1 and 2 in the liquid phase and the corresponding concentrations  $z_1$  and  $z_2$  in the vapour. The concentrations  $x_3$  and  $z_3$  of the third component are given by the relations  $\sum_i x_i = 1$  and  $\sum_i z_i = 1$ . Thus, in addition to temperature and pressure, one concentration may within certain limits be chosen arbitrarily, after which all the other concentrations are fixed by laws of nature.

Since the concentration of one of the components of a homogeneous ternary mixture can always be derived from the other two, it would be quite possible to represent the composition of a ternary mixture on a diagram in rectangular coordinates, one concentration being plotted as ordinates and the other as abscissae. All the compositions of the mixture would then be depicted by the points of an isosceles right-angled triangle, the two equal sides having unit length. For reasons of symmetry it is, however, more usual to use an equilateral triangle. The coordinate axes are then inclined to each other at an angle of  $60^\circ$  and the concentration of the third component can, if desired, be read off directly from the diagram.

Suppose now that, at a certain temperature and a certain pressure,

we fix on a definite concentration  $z_1$  of the first component in the vapour phase. If the concentrations are plotted on the triangular diagram as indicated in Fig. 13 for constant  $T$  and  $p$ , the choice of  $z_1$  fixes two points  $z = (z_1, z_2, z_3)$  and  $x = (x_1, x_2, x_3)$  on this diagram. If we take another value of  $z_1$ , say  $z'_1$ , then  $z_2$  and  $z_3$  will also change, as well as  $x_1$ ,  $x_2$ , and  $x_3$ , and two new points will appear. The loci of all the points  $x$  and  $z$  will in general describe two curves on the triangle, a boiling-curve and a dew-curve. The area between these two curves is the inhomogeneous region. The straight lines joining two points  $x$  and  $z$  that are in equilibrium with each other are called connodals as in the case of binary mixtures.

As a rule, at a given temperature, two-phase equilibrium will not subsist at all if the pressure is lower or higher than the vapour pressures  $\pi_1$ ,  $\pi_2$ ,  $\pi_3$  of all the components at that temperature. If

$$\pi_1 < \pi_2 < p < \pi_3,$$

there will be two-phase equilibrium between 1 and 3 and between 2 and 3, but not between 1 and 2. In this case the curves will cross the triangle in the way indicated in Fig. 14. If  $\pi_1 < p < \pi_2 < \pi_3$ , the curves will run as in Fig. 13.

If at the temperature in question a critical point occurs on the  $(p, x)$  diagram of one of the two-component systems of which the ternary system is composed, say 1 and 3, and if the pressure is higher than the critical pressure of this binary system at the temperature concerned, the dew- and boiling-curves will not traverse the entire diagram but will merge into a single curve, as shown in Fig. 15. When a connodal degenerates to a point, that point is called a critical point of the ternary system. Here liquid and vapour become identical.

Suppose a quantity  $m_y$  of a mixture of the composition  $y_1, y_2, y_3$  be brought to a temperature and pressure corresponding to a point  $y$  in the inhomogeneous region of a triangular diagram. The mixture will separate into a vapour phase  $z$  and a liquid phase  $x$ , and the following four relations will hold:

$$m_y = m_x + m_z,$$

$$m_y y_i = m_x x_i + m_z z_i \quad (i = 1, 2, 3).$$

Hence we can deduce that

$$(z_1 - x_1)/(y_1 - x_1) = (z_2 - x_2)/(y_2 - x_2) = (z_3 - x_3)/(y_3 - x_3).$$

This equation shows that  $y$  lies on a straight line through  $x$  and  $z$  just as in the case of binary systems.

Now let  $x$  and  $z$  be the points marking the phases into which a mixture  $y$  has separated. Then, just as in the case described on p. 18,

$$m_x/m_z = (z_1 - y_1)/(y_1 - x_1) = yz/yx.$$

In order to describe two-phase equilibrium of a ternary system in the way indicated, we need a separate triangle for every temperature

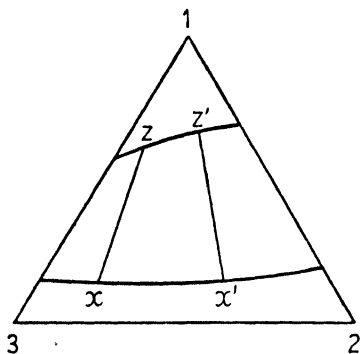


FIG. 13. Equilibrium curves and connodals of ternary mixture

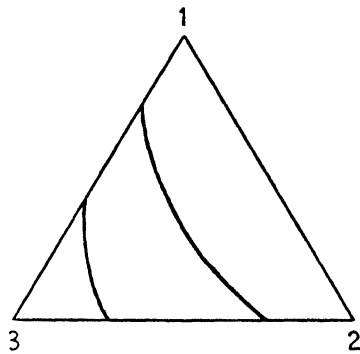


FIG. 14. Equilibrium curves of ternary mixture

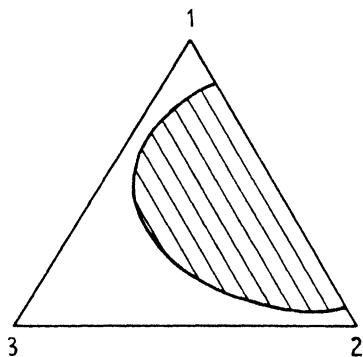


FIG. 15. Equilibrium curves and connodals of ternary mixture showing critical point

and pressure. It is not practicable to plot a whole series of isobars and isothermals on one triangle, as the connodals would intersect and the diagram would be unintelligible.

Hausen† uses a rather more concise triangular diagram. The variables are here taken as  $p$ ,  $z_1$ , and  $z_2$ . At a given pressure, any two values of  $z_1$  and  $z_2$  determine a point  $z$  on the triangle. To given values

† H. Hausen, *Forschung auf dem Gebiete des Ingenieurwesens*, 6, 9 (1935).

of  $z_1$  and  $z_2$  not more than one pair of concentrations  $x_1$  and  $x_2$  will correspond. Within certain limits every point  $z$  will correspond to a point  $x$  with which it is in equilibrium at some temperature or other.

In order to plot all the  $z$ 's and  $x$ 's on one readable diagram Hausen introduces, apart from the ordinary triangular coordinates, which are used to describe the  $z$ 's, a new set of coordinates on the triangle for

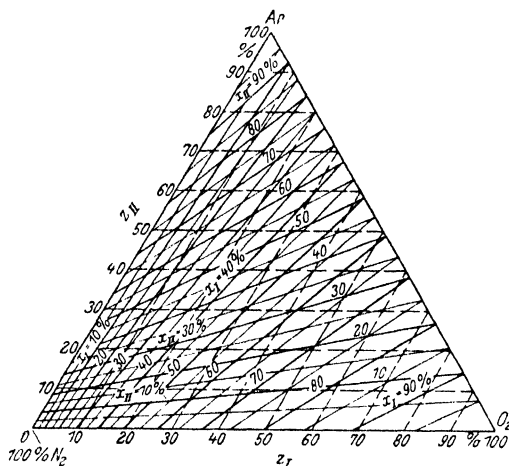


FIG. 16. Equilibrium curves of oxygen-argon-nitrogen mixtures at 1 atm. according to Hausen

$x_I$  per cent. oxygen in liquid  
 $z_I$  per cent. oxygen in vapour  
 $x_{II}$  per cent. argon in liquid  
 $z_{II}$  per cent. argon in vapour

the  $x$ 's in such a way that two corresponding points  $x$  and  $z$  coincide. The new coordinates, which will in general be curved lines, are lines of constant concentration for one of the components in the liquid phase. The two sets of coordinates together describe all the equilibrium states of a ternary system at a given pressure and at all temperatures. However, temperature cannot be read off from this diagram, an example of which is shown in Fig. 16.

A further method of representing ternary mixtures has been used by Fischer.<sup>†</sup> Here a regular orthogonal  $(T, x)$  diagram is used, and equilibrium is shown at constant values of pressure and one concentration. This is achieved with three equilibrium curves in the following way. Let the compositions of the liquid phase be  $x_1, x_2, x_3$  and those of the vapour be  $z_1, z_2, z_3$ , and suppose we have fixed  $x_1 = \text{const.}$  as well as

<sup>†</sup> V. Fischer, *Annalen der Physik*, **21**, 426 (1934).

$p = \text{const.}$  Then the values of  $z_1$  will be given as a function of temperature by the abscissae of one curve, and the values of  $z_2$  will be given by the horizontal distance from this curve to a second curve.  $z_3$  is then simply  $1 - (z_1 + z_2)$ . In the same way the values of  $x_2$  are

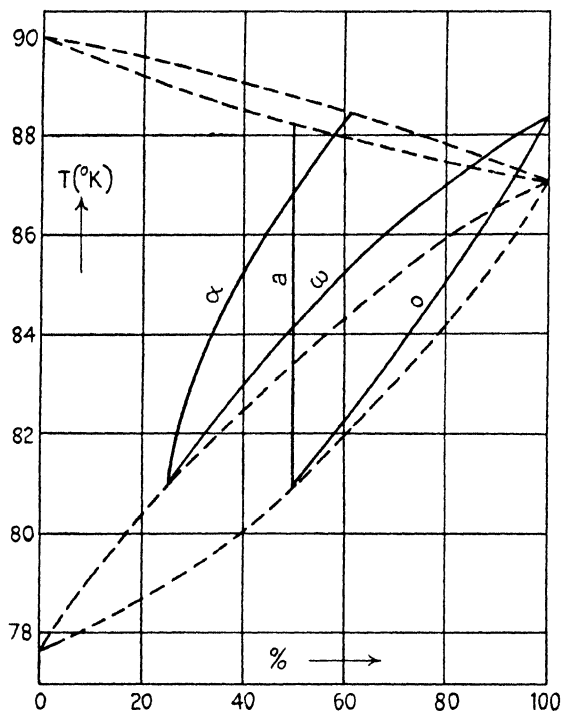


FIG. 17. Equilibrium curves of oxygen-argon-nitrogen mixtures at 1 atm. according to Fischer. Fifty per cent. argon in liquid

o oxygen in liquid      a argon in liquid  
ω oxygen in vapour    α argon in vapour

given by the horizontal distances from the ordinate  $x_1 = \text{const.}$  to a third curve, and  $x_3$  is  $1 - (x_1 + x_2)$ . The curves for the ternary system are bounded by the equilibrium curves of the corresponding binary mixtures.

In Fig. 17 the equilibrium of oxygen-argon-nitrogen mixtures at 1 atm. is represented in this way, as calculated by Fischer, the argon concentration in the liquid being fixed at 50 per cent. The dotted curves represent the oxygen-argon and nitrogen-argon equilibrium.

The principal advantage of this method is that it allows compositions to be read off as a function of temperature. It also enables a whole series of curves for various values of the one fixed concentration to be

plotted on one figure. However, it must be admitted that in this case the diagrams soon become rather confusing, since the curves of one group intersect those of other groups. But the method can be extended to systems of four and more components, which makes it valuable for some calculations.

### 3. Thermodynamic relations†

Hitherto our theoretical considerations have enabled us to determine only the number of independent variables of systems in two-phase equilibrium and the possible general shapes of the curves and surfaces that may, in a  $(p, T, x)$  space and its  $(p, x)$  and  $(T, x)$  sections, represent the boundaries between liquid and gaseous phases. It is in the nature of thermodynamics that it can give us no quantitative information as to the exact form of these curves and surfaces. This information, which is contained in equations of state, can be deduced only from molecular theory. The existing equations of state for liquid and gaseous mixtures are either too inaccurate to give the required results except in particular cases, or they contain so many specific constants that their use presupposes the existence of extensive experimental data concerning the mixtures in question. As a result of this, it has been necessary to determine the  $(p, T, x)$  relations of liquid mixtures in equilibrium with their vapours on the basis of direct experiment.

Nevertheless, especially at low pressures, when the state of the vapour is not too far removed from that of a perfect gas, some theoretical conclusions can be drawn. It was stated in §1 that a liquid and a vapour cannot be in equilibrium with one another unless the temperature and the pressure are the same in both phases. The laws of thermodynamics require yet a third condition to be fulfilled in the case of mixtures containing more than one component, and this is that the chemical potential  $\mu_i$  of each component  $i$  shall be the same in both phases. One of several alternative definitions of the chemical potential is by the relation

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,p}, \quad (1)$$

where  $n_i$  is the number of moles of the component  $i$  in the particular phase and  $G$  is the Gibbs potential, which is related to the energy  $E$  and the entropy  $S$  by the equation

$$G = E - TS + pV. \quad (2)$$

† For the thermodynamics of mixtures and solutions see E. A. Guggenheim, *Modern Thermodynamics by the Methods of Willard Gibbs*. Methuen, 1933.

As we shall in future never use  $E$  in our calculations, but shall frequently require the enthalpy  $H$ , which is defined as

$$H = E + pV, \quad (3)$$

we can best write equation (2) in the form

$$G = H - TS. \quad (4)$$

$G$  is here considered as a function of  $p$ ,  $T$ , and the  $n_i$ , so that

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial p} dp + \sum_i \frac{\partial G}{\partial n_i} dn_i, \quad (5)$$

for which we may write, using (1) and well-known thermodynamic relations,

$$dG = -SdT + Vdp + \sum \mu_i dn_i. \quad (6)$$

Now consider a change at constant temperature and pressure in which the number of moles of each component is increased by the same fraction  $d\lambda$  of the number already present, so that

$$dn_i = n_i d\lambda.$$

The composition of the mixture thus remains unaltered and, as temperature and pressure do not change, all those properties of the system, such as volume, enthalpy, entropy, etc., whose values for the whole system are equal to the sum of their values for its parts, will also increase by a factor equal to  $d\lambda$  times their original values. Since the Gibbs potential is such a property,

$$dG = Gd\lambda.$$

But for a change at constant temperature and pressure equation (6) gives  $dG = \sum_i \mu_i dn_i$ , and this is equal to  $\sum \mu_i n_i d\lambda$ , so that

$$dG = \sum_i \mu_i n_i d\lambda.$$

Equating coefficients, we thus obtain

$$G = \sum_i \mu_i n_i, \quad (7)$$

a relation which is evidently independent of the fact that the change we considered took place at constant temperature and pressure. Therefore

$$dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i. \quad (8)$$

By comparing (8) with (6) we obtain

$$-SdT + Vdp - \sum_i n_i d\mu_i = 0. \quad (9)$$

This gives a relation, valid in any phase, between changes of pressure,



temperature, and composition. For the special case of isothermal changes at constant pressure

$$\sum_i n_i d\mu_i = 0. \quad (10)$$

This is known as the Gibbs-Duhem relation.

For the case of equilibrium between a liquid phase  $L$  and a vapour phase  $G$ , we have two equations of the form of (9). By subtracting one from the other we obtain

$$-(S_G - S_L) dT + (V_G - V_L) dp - \sum_i (n_{Gi} - n_{Li}) d\mu_i = 0, \quad (11)$$

since

$$\mu_{Li} = \mu_{Gi} = \mu_i.$$

For an isothermal change in a binary system we thus have

$$(V_G - V_L) dp - (n_{G1} - n_{L1}) d\mu_1 - (n_{G2} - n_{L2}) d\mu_2 = 0. \quad (12)$$

Replacing the  $n_i$  by mole fractions  $x = n_{L1}/(n_1 + n_2)$  and  $z = n_{G1}/(n_1 + n_2)$  and the volumes  $V$  by molal volumes  $v = V/(n_1 + n_2)$ , this equation becomes

$$(v_G - v_L) dp - (z - x)(d\mu_1 - d\mu_2) = 0. \quad (13)$$

In order to make use of these equations, we must know  $\mu_1$  and  $\mu_2$  as functions of pressure and composition. It is here that we must add to our thermodynamic relations knowledge obtained from an equation of state. From here on the equations are therefore no longer of general validity.

The chemical potential  $\mu_i$  of a component in a perfect gas mixture may be written in the form

$$\mu_i = \mu_i^0(T) + RT \log p_i, \quad (14)$$

where  $\mu_i^0(T)$  depends on the temperature alone and  $p_i$  is the partial pressure of the  $i$ th component defined by

$$p_i = x_i p. \quad (15)$$

Then at constant temperature

$$d\mu_i = RT d \log p_i, \quad (16)$$

and if we replace moles by mole fractions, equation (10) reads

$$\sum_i x_i d \log p_i = 0, \quad (17)$$

valid for constant temperature and total pressure. This is known as the Duhem-Margules relation. Since the  $\mu_i$  of a liquid in equilibrium with a vapour are the same as those of the vapour itself, equation (16) will also hold for a liquid in equilibrium with a perfect gaseous mixture. The  $p_i$  are then partial vapour pressures.

Equation (13) may then be written

$$(v_G - v_L) dp = (z - x) RT (d \log p_1 - d \log p_2). \quad (18)$$

If we write  $p_1 = zp$ ,  $p_2 = (1 - z)p$ , (18) becomes

$$(v_G - v_L) dp = RT \frac{z - x}{z(1 - z)} dz. \quad (19)$$

When, as here, the vapour is a perfect gas, we may frequently assume that the pressure is so low that the specific volume of the liquid may be neglected as compared with that of the gas. Then the left side of (19) becomes  $v_G dp = RT d \log p$ , and we obtain

$$d \log p = \frac{z - x}{z(1 - z)} dz, \quad (20)$$

valid for changes at constant temperature. This equation can be integrated according to a method proposed by Runge. It can then be used to calculate the dew-curve  $z(p)$  of a binary mixture when the boiling-curve  $x(p)$  is known. It should be remembered that (20) holds only at low pressures when the vapour may be considered to be a perfect gas and the molal volume of the liquid may be neglected.

If the vapour is not a perfect gas, the chemical potential  $\mu_i$  may be written

$$\mu_i = \mu_i^0(T) + RT \log p_i^*, \quad (21)$$

where  $p_i^*$  is the fugacity, as defined by this equation, and the relation  $p_i^* \rightarrow p_i$  when  $p \rightarrow 0$ . The value of  $p_i^{*0}$  for a pure component may be obtained, according to Lewis, with the help of the equation of state of that component from the relation

$$RT \log p^{*0} = RT \log p + \int_0^p (v - v^*) dp, \quad (22)$$

where  $v^*$  is the volume which 1 mole of the gas would occupy at the pressure  $p$  if it were a perfect gas. If the pressure is not too high,  $p_i^*$  can be determined from the empirical relation

$$p_i^* = p_i^{*0} z_i. \quad (23)$$

Calculations based on equations (17) and (18) can then be applied to systems with imperfect vapour phases by substituting  $p_i^*$  for  $p_i$ .

The chemical potentials of a number of liquid mixtures conform to the equation

$$\mu_{iL} = \mu_{iL}^0 + RT \log x_i, \quad (24)$$

where  $\mu_{iL}^0$  depends on temperature and pressure but not on composition. These mixtures are known as 'perfect solutions'.

Now for a vapour in equilibrium with a liquid  $\mu_{iL} = \mu_{iG}$ . If the vapour is a perfect gas,  $\mu_{iG} = RT d \log p_i$ , and hence

$$\log p_i = \log x_i + \log k_i,$$

where  $k_i$  is independent of composition. When  $x_i \rightarrow 1$ ,  $p_i \rightarrow \pi_i$ , where  $\pi_i$  is the vapour pressure of the pure  $i$ th component. Therefore  $k_i = \pi_i$  and

$$p_i = \pi_i x_i. \quad (25)$$

That is to say, the partial pressure of the  $i$ th component in the vapour is equal to the vapour pressure of the pure component multiplied by

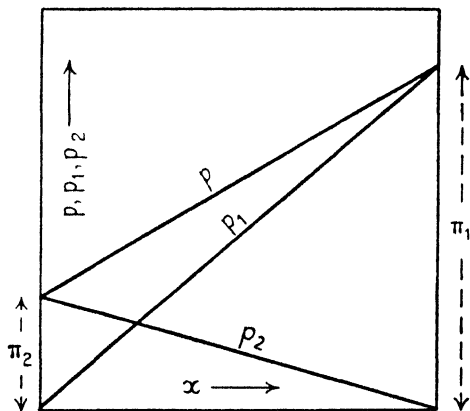


FIG. 18. Partial and total pressures of perfect binary solution

the concentration of that component in the liquid phase (Fig. 18). Equation (25) is known as Raoult's law, which is valid for all solutions at sufficiently low concentrations. Perfect solutions are thus solutions for which Raoult's law holds for all concentrations.

If the vapour phase is not a perfect gas, a solution may yet be defined as perfect if it conforms to the equation

$$p_i^* = p_i^{*0} x_i, \quad (26)$$

where  $x_i$  is again the concentration of the  $i$ th component in the liquid phase,  $p_i^{*0}$  is the fugacity of the pure  $i$ th component at the particular temperature and at the saturation pressure corresponding to that temperature, and  $p_i^*$  is the fugacity of the  $i$ th component in the gaseous mixture. Equation (26) is a perfectly justifiable generalization of the definition of a perfect solution, but it is unsatisfactory in that we have no adequate means of determining  $p_i^*$ , unless, as is rarely the case, extensive ( $p, v, T$ ) data are available for the mixture in question. For

not very high pressures Lewis and Randall† found that the fugacity of a gas in a mixture was equal to its concentration multiplied by the fugacity of the pure gas at the temperature and total pressure of the mixture. This empirical rule is contained in the equation

$$p_i^* = p_i^{*0} z_i, \quad (23)$$

which enables  $p_i^*$  to be computed and equation (26) to be checked. It should be noted that in (26)  $p_i^{*0}$  is a constant for a given temperature,

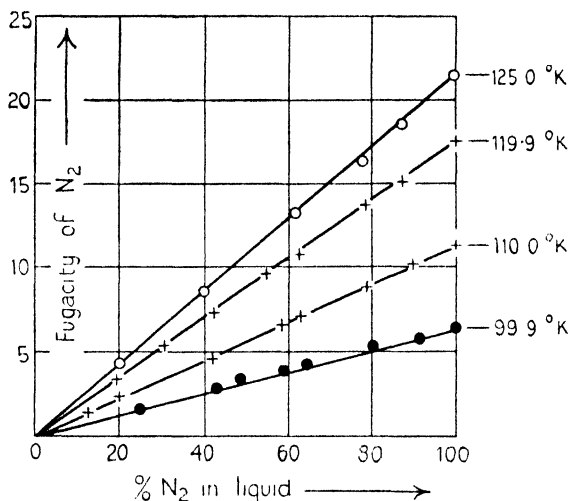


FIG. 19. Fugacity of nitrogen in nitrogen-oxygen mixtures

whereas in (23) it is a function of the pressure, which itself depends on  $z_i$ .

Krichevsky and Torocheshnikov‡ showed that mixtures of oxygen and nitrogen and of carbon monoxide and nitrogen could be described accurately by equation (26) up to pressures close to the critical, whereas (25) failed at comparatively low pressures. Fig. 19 shows the fugacity of nitrogen in oxygen-nitrogen mixtures as a function of concentration according to the calculations of Krichevsky and Torocheshnikov. In Fig. 20 the partial pressures are shown to be very far from linear. In the case of oxygen-nitrogen mixtures the experimental data are taken from Dodge and Dunbar's|| paper; the

† G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, 1923, p. 226.

‡ J. Krichevsky and N. Torocheshnikov, *Zeitschr. f. phys. Chemie (A)*, **176**, 338 (1936).

|| B. F. Dodge and A. Dunbar, *J. Amer. Chem. Soc.* **49**, 591 (1927).

nitrogen-carbon monoxide data are from Torocheshnikov's† own experiments.

In the case of perfect solutions, all the properties of the mixture can be calculated from data applying to the pure components and can be expressed in simple formulae involving pressure or fugacity, according

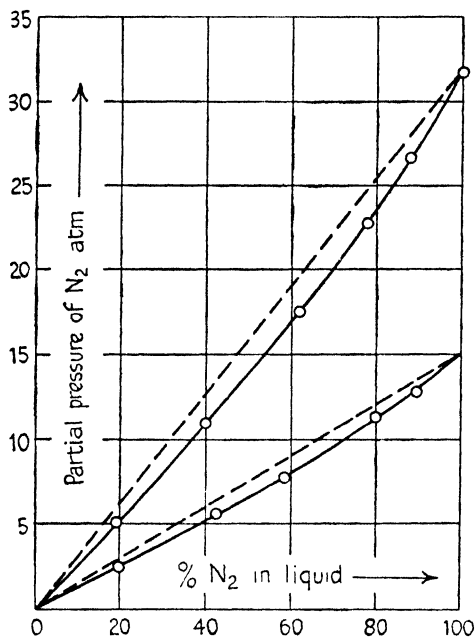


FIG. 20. Partial pressure of nitrogen in nitrogen-oxygen mixtures

to whether the vapour phase may or may not be considered as a perfect gas.‡

When the vapour is a perfect gas, then, as we have seen, the total pressure is a linear function of the composition of the liquid phase. This means that the boiling-curve of a perfect binary solution in a  $(p, x)$  diagram is a straight line. The shape of the dew-curve will be obtained by considering the total pressure  $p$  as a function of the composition  $z$  of the vapour. From (25) we obtain

$$p = \pi_1 x_1 + \pi_2 (1 - x_1). \quad (27)$$

Moreover, since (25) requires the vapour to be a perfect gas,

$$p_1 = z_1 p, \quad p_2 = (1 - z_1) p;$$

† N. Yushkevich and N. Torocheshnikov, *Zhurnal khimicheskoi Promyshlennosti*, 13, No. 21 (1936).

‡ See H. Hausen, 'Materialtrennung durch Destillation und Rektifikation', *Der Chemie-Ingenieur*, I, part 3, ch. 15, p. 70 et seq. Leipzig, 1933.

so with

$$p_1 = x_1 \pi_1, \quad p_2 = (1-x_1)\pi_2,$$

$$\frac{z_1}{1-z_1} = \frac{x_1}{1-x_1} \frac{\pi_1}{\pi_2}. \quad (28)$$

Solving (28) for  $x_1$ , we obtain

$$x_1 = \frac{z_1 \pi_2}{\pi_1 - (\pi_1 - \pi_2)z_1}. \quad (29)$$

Inserting this in (27), we find

$$p = \frac{\pi_1 \pi_2}{\pi_1 - (\pi_1 - \pi_2)z_1}. \quad (30)$$

The curve depicting pressure as a function of the composition of the vapour phase, i.e. the dew-curve, is therefore part of a hyperbola. The  $(p, x)$  diagram of a perfect solution, the vapour of which is a perfect gas, is thus shaped as in Fig. 21, and may be quantitatively deduced if the vapour pressures of the two components are known at the temperature concerned.

In order to deduce the  $(T, x)$  diagram of a perfect solution, again assuming the vapour to be a perfect gas, we may solve (27) and (30) for  $x_1$  and  $z_1$  respectively, obtaining

$$x_1 = \frac{p - \pi_2}{\pi_1 - \pi_2} \quad (31)$$

and

$$z_1 = \pi_1 x_1 / p. \quad (32)$$

If we know  $\pi_1$  and  $\pi_2$  as functions of  $T$  we can calculate the  $(T, x)$  curves for constant  $p$ .

Finally, we can obtain the *concentration curve*  $z_1$  as a function of  $x_1$  from equation (28), which gives

$$z_1 = \frac{\pi_1 x_1}{\pi_2 + (\pi_1 - \pi_2)x_1}, \quad (33)$$

or, if  $\pi_1/\pi_2 = \epsilon$ ,

$$z_1 = \frac{\epsilon x_1}{1 + (\epsilon - 1)x_1}. \quad (34)$$

This curve is of the type shown in Fig. 22. The greater  $\epsilon$ , the more it differs from the diagonal. If, in the interval of temperature concerned,  $\epsilon$  may be considered as constant, the curve is a hyperbola.

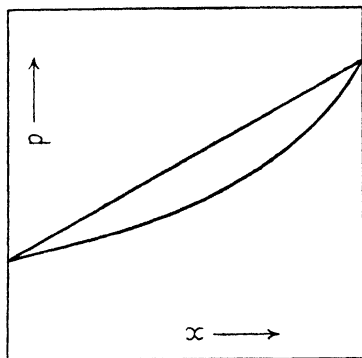


FIG. 21.  $(p, x)$  curves of perfect solution

In the case of ternary mixtures, the problem is to find the dew- and boiling-curves at constant  $T$  and  $p$  which describe the states the system passes through when one of the components is varied. Let the concentrations of the liquid be  $x_1, x_2, x_3$ , and those of the vapour phase be

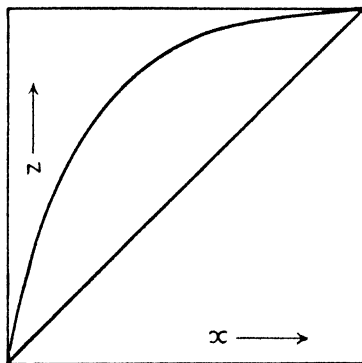


FIG. 22. Concentration curve of perfect solution  
 $x$  concentration of more volatile component in liquid  
 $z$  concentration of more volatile component in vapour  
 The diagonal is shown for comparison

$z_1, z_2, z_3$ , and suppose  $z_1$  to be arbitrarily chosen and varied. When the vapour is a perfect gas we may again use

$$p_i = x_i \pi_i. \quad (25)$$

With

$$p_i = z_i p \quad (35)$$

this gives

$$x_1 = z_1 p / \pi_1. \quad (36)$$

From (25) we obtain

$$p = \sum_i x_i \pi_i, \quad (27)$$

from which  $x_3$  may be eliminated with the relation  $\sum_i x_i = 1$ . This gives

$$x_2 = \frac{p - \pi_3 + x_1(\pi_3 - \pi_1)}{\pi_2 - \pi_3}. \quad (37)$$

Finally, from (25) and (35),

$$z_2 = z_1 x_2 \pi_2 / x_1 \pi_1. \quad (38)$$

Equations (36), (37), and (38), together with the relations

$$x_3 = 1 - x_1 - x_2 \quad \text{and} \quad z_3 = 1 - z_1 - z_2,$$

enable us to compute all the concentrations in both phases as functions of  $z_1$  when the vapour pressures of the pure components are known at the temperature in question. For perfect solutions the series of triangles describing equilibrium at various temperatures and pressures can thus be deduced.

To obtain Hausen's triangles for variable temperature, with their two systems of coordinates, we have only to solve (36) for  $z_1$  and the corresponding equation for  $z_2$  and insert the value of  $p$  from (27). If we put  $\pi_1/\pi_3 = \epsilon_1$  and  $\pi_2/\pi_3 = \epsilon_2$  we obtain the two equations

$$z_1 = \frac{\epsilon_1 x_1}{1 + (\epsilon_1 - 1)x_1 + (\epsilon_2 - 1)x_2}, \quad z_2 = \frac{\epsilon_2 x_2}{1 + (\epsilon_1 - 1)x_1 + (\epsilon_2 - 1)x_2}, \quad (39)$$

which enable us everywhere to compute  $x_1, x_2, x_3$  when  $z_1, z_2, z_3$  are given. For these perfect solutions the coordinates  $x_1 = \text{const.}$  and  $x_2 = \text{const.}$  are evidently straight lines.

#### 4. The determination of equilibrium curves

The experimental material on the equilibrium of binary and ternary mixtures of low-boiling substances is still comparatively scarce and most of it is of very recent date. Only ten years ago the only system which had been investigated in detail was oxygen and nitrogen. Even now not nearly all the systems that are important in the separation of gases have been studied.

The reason for this scarcity of data is to be sought in the very considerable experimental difficulties that are incurred when a mixture is to be brought to exact equilibrium under well-defined conditions of pressure and temperature. The determinations that have to be made in studying equilibria are those of pressure, temperature, and composition. Methods for measuring pressure and temperature have been well developed long ago and here we meet with no overwhelming obstacles. Pressures are usually determined with mercury manometers at low and moderate values, and higher pressures are measured with Bourdon gauges. These secondary manometers must be recalibrated frequently with a pressure balance. In accurate experiments it is advisable to employ a pressure balance directly without having recourse to Bourdon gauges at all.

For measuring temperature all the four well-known low-temperature methods have been successfully applied: gas thermometers, vapour-pressure thermometers, thermo-couples, and resistance thermometers. Vapour-pressure and resistance thermometers are probably the best suited for this purpose.

The composition of the mixture is generally determined by the classical methods of gas analysis. These methods are mostly cumbersome and require a considerable time for each test. The measurements



are thus greatly protracted, since it is usually necessary to analyse a number of mixtures in each experiment. There are two ways out of this difficulty: firstly, methods of determining equilibrium can be devised in which no analyses need be made; secondly, physical methods may be employed to analyse the mixtures. These methods, though they often require rather a complicated equipment, are frequently more accurate than chemical determinations and require less time. In some cases it is possible to analyse a stream of gas continuously, which greatly increases the accuracy of the results and considerably shortens the time needed to perform the experiment.

The accurate and swift determination of gas composition is only one of the difficulties encountered in these experiments. The second and more serious problem consists in bringing a mixture to a state of actual phase equilibrium. Unless very great precautions are taken a liquid and a gaseous mixture under fixed conditions of pressure and temperature will remain for long periods of time in a state more or less removed from true equilibrium. This is mainly due to the low coefficients of diffusion and heat transfer and to the fact that small drops of liquid are frequently present in the gaseous phase, whereas they are not noticeable as such in the analysis. As a result, the compositions of gas and liquid actually determined differ from each other less than under real equilibrium conditions. The inhomogeneous regions thus appear narrower than they should.

A number of 'simplified' methods of determining liquid-vapour equilibrium have been put forward from time to time, but they have almost all had to be discarded in favour of more cumbersome methods, as the results were not sufficiently accurate.

The methods for investigating liquid-vapour equilibrium can be divided roughly into the following groups.

1. **Dew- and boiling-point method.** A gas of known composition is introduced into an equilibrium vessel at constant temperature. The pressure is observed at which condensation commences and is completed.

This method was developed by Kuenen at Leiden and has been frequently employed. It was used by Holst and Hamburger† on argon-nitrogen mixtures, by Bourbo and Ischkin‡ on mixtures of argon and oxygen, and by Steckel|| on nitrogen-carbon monoxide mixtures. It

† G. Holst and L. Hamburger, *Zeitschr. f. phys. Chemie*, **91**, 513 (1916).

‡ P. Bourbo and I. Ischkin, *Phys. Zeitschr. d. Sowjetunion*, **10**, 271 (1936).

|| F. Steckel, *ibid.* **8**, 337 (1935).

has been developed to considerable perfection in recent years by Sage and Lacey,<sup>†</sup> who used it for mixtures of light hydrocarbons, chiefly above room-temperature. The method has the advantage that the phases need not be analysed, since the mixtures may be composed arbitrarily, but it must be applied with great care if accurate results are to be obtained.

**2. Static method.** A mixture is confined in the equilibrium vessel at constant temperature and pressure corresponding to a point in the inhomogeneous region of the phase diagram. The *composition* of the liquid and vapour phases is determined.

The static method was used by Verschoyle<sup>‡</sup> on nitrogen–hydrogen, carbon monoxide–hydrogen, and the ternary system nitrogen–carbon monoxide–hydrogen, by Freeth and Verschoyle<sup>||</sup> for hydrogen–methane mixtures, and by Fedoritenko and Ruhemann<sup>††</sup> for mixtures of nitrogen and helium.

It is a useful and fairly accurate method for high and moderate pressures, especially when the temperature is above the critical point of one of the components. Its chief disadvantage is that equilibrium is apt to be destroyed when analysis tests are taken. It is this that renders the method inaccurate at low pressures, since here the amount of gas needed for the analysis is of the order of magnitude of the total quantity of gaseous phase present in the equilibrium vessel.

**3. Flow method.** The mixture is passed slowly and continuously at constant pressure through an apparatus that is constructed so as to ensure good thermal contact with the liquid in the cryostat. The gaseous phase flows into a gasometer, the liquid collecting in a receptacle below the equilibrium apparatus. The gas in the gasometer is *analysed* at the end of the experiment as well as a portion of the liquid phase. In some cases gas and liquid are analysed continuously during the run.

The method has been used by Steckel and Zinn<sup>‡‡</sup> with the system hydrogen–nitrogen–methane, by Ruhemann and Zinn<sup>||||</sup> with hydrogen–nitrogen–carbon monoxide, by Fedoritenko and Ruhemann<sup>††</sup> with nitrogen and helium, by Ruhemann<sup>†††</sup> for mixtures of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ,

<sup>†</sup> B. H. Sage and W. N. Lacey, *Ind. Eng. Chemistry*, **26**, 103, 214 (1934).

<sup>‡</sup> T. T. H. Verschoyle, *Trans. Roy. Soc. (A)*, **230**, 189 (1931).

<sup>||</sup> F. A. Freeth and T. T. H. Verschoyle, *Proc. Roy. Soc. (A)*, **130**, 453 (1931).

<sup>††</sup> A. Fedoritenko and M. Ruhemann, *Techn. Phys. of U.S.S.R.* **4**, 1 (1937).

<sup>‡‡</sup> F. Steckel and N. Zinn, *Zhurnal khimicheskoi Promyshlennosti*, **16**, No. 8 (1939).

<sup>||||</sup> M. Ruhemann and N. Zinn, *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937).

<sup>†††</sup> M. Ruhemann, *Proc. Roy. Soc. (A)*, **171**, 121 (1939).

and by Guter, Newitt, and Ruhemann† for  $\text{CH}_4\text{--C}_2\text{H}_4$  mixtures. If properly handled it is reliable and gives quite accurate results. It is suitable for high and medium pressures, but is not very good in the critical region. There is a considerable danger of the equilibrium vessel becoming swamped, owing to too rapid condensation.

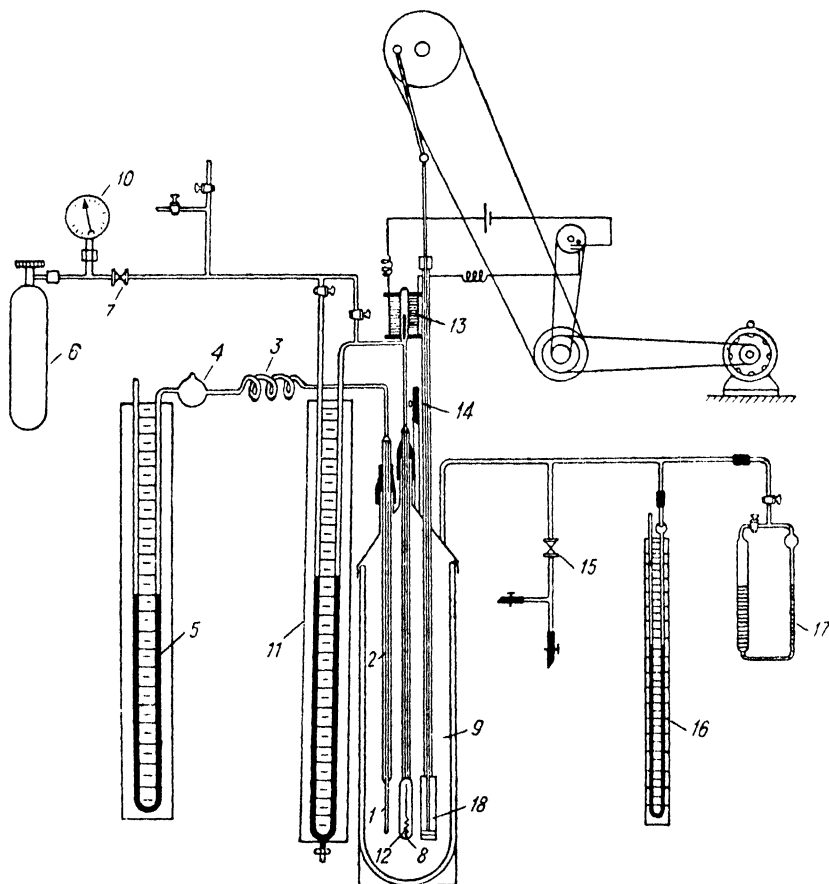


FIG. 23. Apparatus for boiling-point method‡

4. **Circulation method.** A gaseous mixture is circulated through the liquid in the equilibrium vessel by a small pump at constant pressure and temperature. In course of time liquid and gas assume equilibrium. Both phases are *analysed* from time to time until the analysis tests give constant results.

† M. Guter, D. M. Newitt, and M. Ruhemann, *Proc. Roy. Soc. (A)*, in the press.

‡ P. Bourbo and I. Ischkin, *Phys. Zeitschr. d. Sowjetunion*, **10**, 271 (1936).

This method was developed by Dodge and Dunbar† in their work on oxygen–nitrogen mixtures. It has recently been employed by Torocheshnikov‡ in studying the equilibrium of the carbon monoxide–nitrogen system. It is probably the most accurate and reliable of all existing methods but demands a rather elaborate and complicated equipment.

Fig. 23 shows the apparatus of type (1) used by Bourbo and Ischkin for studying mixtures of oxygen and argon at low pressures. The mixture of known composition is transmitted from the cylinder 6 through the valve 7 to the glass equilibrium vessel 8 of about 8 c.c. capacity, immersed in the cryostat 9, which is filled with liquid oxygen. The cryostat is a copper Dewar vessel of 2 litres capacity and is fitted with a mechanical stirrer 18. The temperature in the cryostat is read with an oxygen vapour-pressure thermometer 1 on a mercury manometer 5. 1 is placed immediately beside 8 and the tube 2 connecting it to 5 is insulated from the liquid in the cryostat, as a vertical temperature head in the cryostat would influence the readings of the thermometer. The temperature in the cryostat is adjusted by pumping off the vapour and regulating valve 15 with the help of a mercury manometer 16 and a differential manometer 17 filled with a light oil. The equilibrium vessel is equipped with a light stirrer 12 operated with an electromagnet 13. The pressure in the equilibrium vessel is read on the mercury manometer 11.

In the experiments of Bourbo and Ischkin only the boiling-points were determined, i.e. the pressures at which mixtures of different concentrations completely condensed. The corresponding dew-curves were computed by solving the Duhem-Margules equation according to Runge's method, as mentioned on p. 29.

Fig. 24 gives a sketch of an apparatus of the same type (1) used by Steckel on nitrogen–carbon monoxide mixtures at pressures up to 17 atm. The copper equilibrium vessel II is fitted with a vapour-pressure thermometer III and suspended from a German silver capillary K in a copper cryostat I, the temperature of which can be varied as in

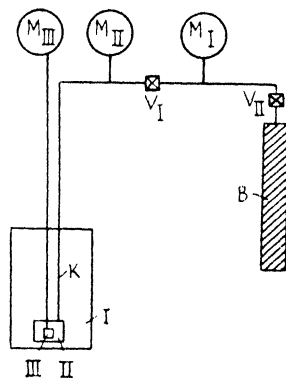


FIG. 24. Arrangement for dew- and boiling-point method

† B. F. Dodge and A. Dunbar, *J. Amer. Chem. Soc.* **49**, 591 (1927).

‡ N. Torocheshnikov, *Journ. Techn. Phys.* (Russian), **7**, 1107 (1937).

the apparatus just described. A steel cylinder  $B$  containing the mixture of known composition is connected with II through valves  $V_I$  and  $V_{II}$ , separated by a narrow tube and a Bourdon gauge  $M_I$ . The pressure in II is read on  $M_{II}$ . The space between  $V_I$  and  $V_{II}$  is filled with gas at the pressure of the cylinder and is then transferred in small portions through  $V_I$  to the equilibrium vessel,  $V_{II}$  being closed.  $M_{II}$  is

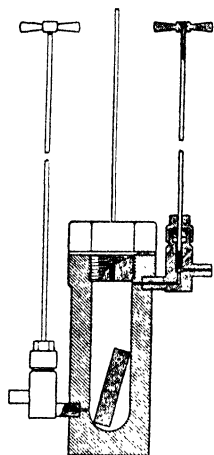


FIG. 25. Equilibrium vessel for static method

read as a function of  $M_I$ . As the volume between  $V_I$  and  $V_{II}$  consists mainly of  $M_I$  itself, the readings of  $M_I$  are a sensitive measure of the volume of gas passed into II. As long as no condensation occurs, a straight line is obtained by plotting the readings of  $M_{II}$  against those of  $M_I$ . At the dew-point this line shows a marked kink, since the condensation retards the rise of pressure in II. When II is completely filled with liquid another still more pronounced kink is observed as the pressure in II now rises rapidly when small portions of gas are added owing to the small compressibility of the liquid.

This apparatus is exceedingly simple but not very reliable, as one can never be quite certain that equilibrium in II has actually been attained.

Fig. 25 shows the equilibrium vessel used by Verschoyle for his static method (2), in studying the equilibrium of hydrogen-nitrogen-carbon monoxide at pressures up to 225 atm. The vessel is of brass and has a volume of 9 c.c. The mixture is admitted through the central capillary tube. The analysis tests are taken through the two lateral outlets, fitted with specially constructed taps that work at low temperatures. The spindles of the taps extend through the cover of the cryostat, so that they may be operated at room-temperature. The glands of the taps, which gave the author considerable trouble, were of well-dried cork and could be made vacuum-tight after long usage. The equilibrium vessel is fitted with a stirrer consisting of an iron cylinder, which is kept in motion with the help of an electromagnet placed outside the cryostat.

In Fig. 26 a sketch is given of the apparatus constructed by Steckel and Zinn according to the flow method (3), and used up to 100 atm. in studying mixtures of hydrogen, nitrogen, and methane. A similar apparatus was used by Guter, Newitt, and Ruhemann and for investigating methane-ethane and methane-ethylene mixtures and mixtures of methane-ethylene-ethane. The mixture is passed very slowly through

a bundle of copper capillary tubes of 2 mm. outer diameter and 1 mm. inner diameter, which are immersed in the cryostat. The liquid-gaseous mixture, which is formed in the capillaries, enters the receiver, the liquid collecting in the conical bottom of the vessel, and the gas passing out through the tube  $T_2$ . The mixture entering the receiver is directed so as to strike the walls, thus increasing the surface of contact and giving the liquid a good chance of trickling down into the base. A piece of copper wire netting  $G$  is placed below the exit at the top of the receiver to catch any drops of liquid that may be carried away by the vapour. During the run the pressure is maintained constant, the liquid gradually collecting. The vapour phase is passed out continuously through a valve, which is connected to the gasometer when it may be assumed that a stationary state has been reached. The analysis test of the liquid is taken through a valve attached to  $T_1$  at the end of the run, the pressure being maintained constant during the operation.

Fig. 27 shows the equipment used by Dodge and Dunbar† on oxygen-nitrogen mixtures. The circulation method (4) was used. By means of the mercury-column circulating-pump  $C$  vapour is taken from the equilibrium chamber  $N$  through a heat-exchanger  $I$ , a valve  $W$ , a reservoir  $X$ , and back to  $N$  again. In the figure  $J$  and  $K$  are storage cylinders for oxygen and nitrogen;  $O$  is a piston pressure balance with an equilibrium indicator  $d$ ;  $Y$  and  $Z$  are mercury burettes to enable samples of liquid and vapour to be taken. Liquid oxygen for the bath is forced out of the metal vacuum vessel  $P$  into the cryostat  $M$ , where its temperature is kept

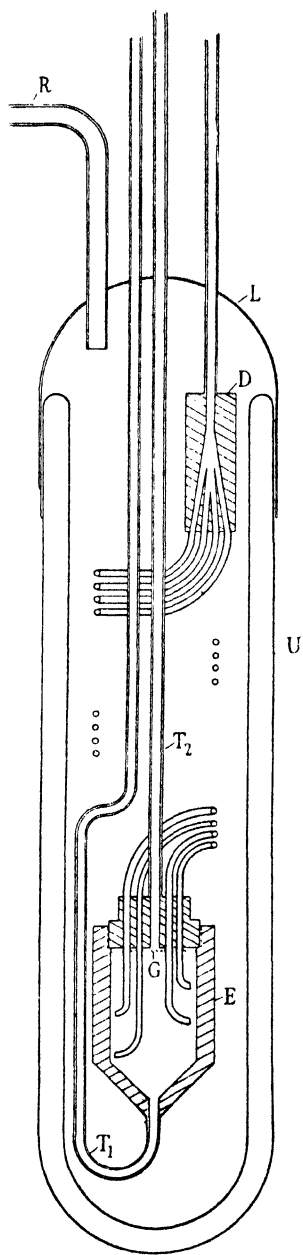


FIG. 26. Equilibrium vessel and cryostat for flow method

† B. F. Dodge and A. K. Dunbar, *Journ. Amer. Chem. Soc.* **49**, 591 (1927).

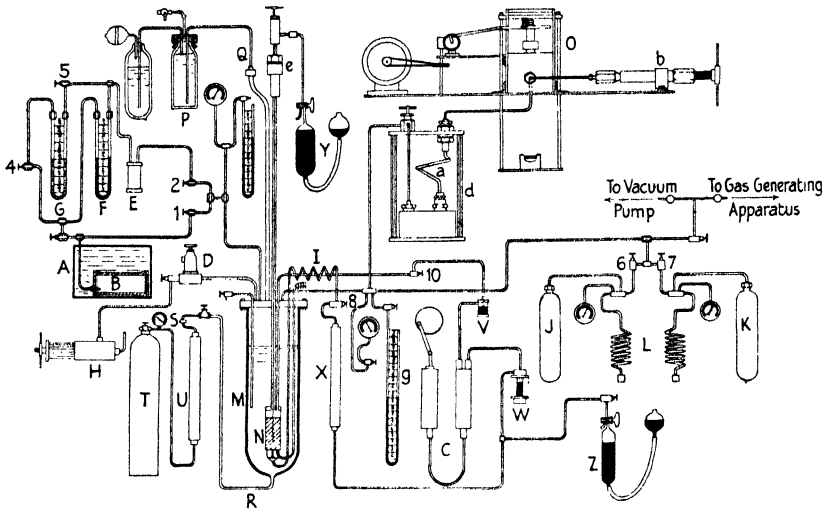


FIG. 27. Apparatus for circulation method

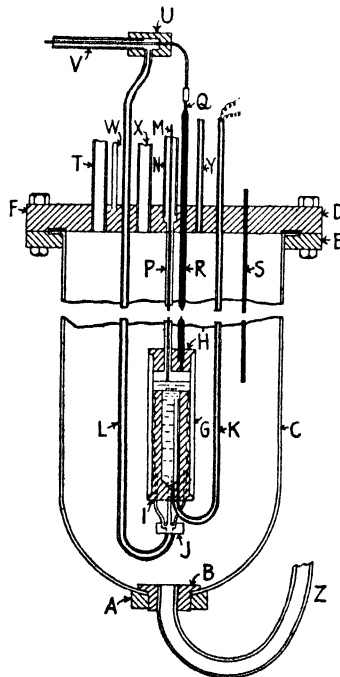


FIG. 28. Cryostat and equilibrium vessel for circulation method

constant by means of an 'artificial atmosphere' maintained in the cylinder *B* and regulated with the plunger valve *H* and the differential manometers *F* and *G*, filled with mercury and oil respectively. The cryostat and equilibrium vessel are shown separately in Fig. 28. Gas is admitted through the tube *L* and the manifold *J*, which conducts it in three separate currents to three threads, cut on the outside of the copper piece *I* inside the brass tube *G*. This arrangement ensures adequate mixing of vapour and liquid.

## 5. Survey of experimental results

The following figures show the equilibrium curves of those binary and ternary mixtures that have been investigated up to date, the components of which are gaseous at room temperature and atmospheric pressure. Where possible  $(p, x)$  and  $(T, x)$  curves are shown. Authors' names and references are given and the type of apparatus is mentioned with which the experiments were carried out.



# Oxygen-Nitrogen

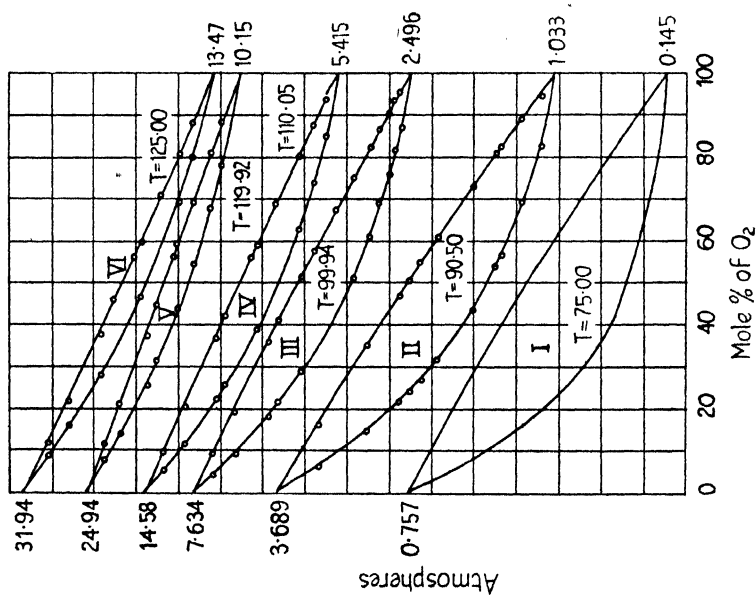


Fig. 29. ( $p, x$ ) curves at 75.00, 90.50, 99.94, 110.05, 119.92, and 125.00° K. Dodge and Dunbar, 'Circulation Method', *Journ. Amer. Chem. Soc.* 49, 591 (1927)

# Oxygen-Nitrogen

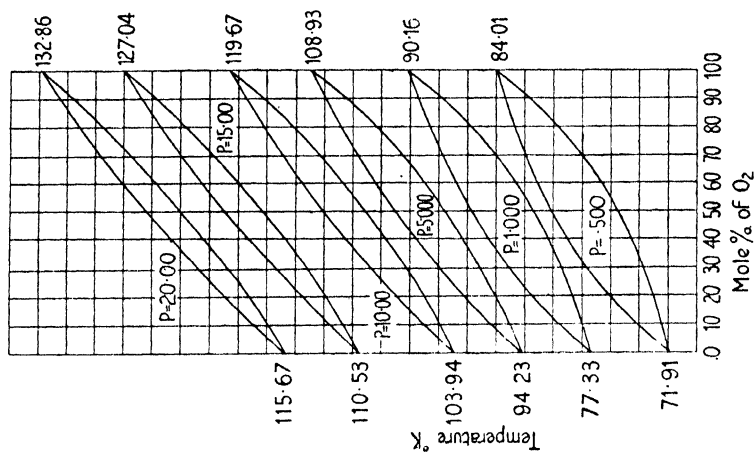


Fig. 30. ( $T, x$ ) curves at 0.5, 1, 5, 10, 15, and 20 atm. Dodge and Dunbar, 'Circulation Method' (see Fig. 29)

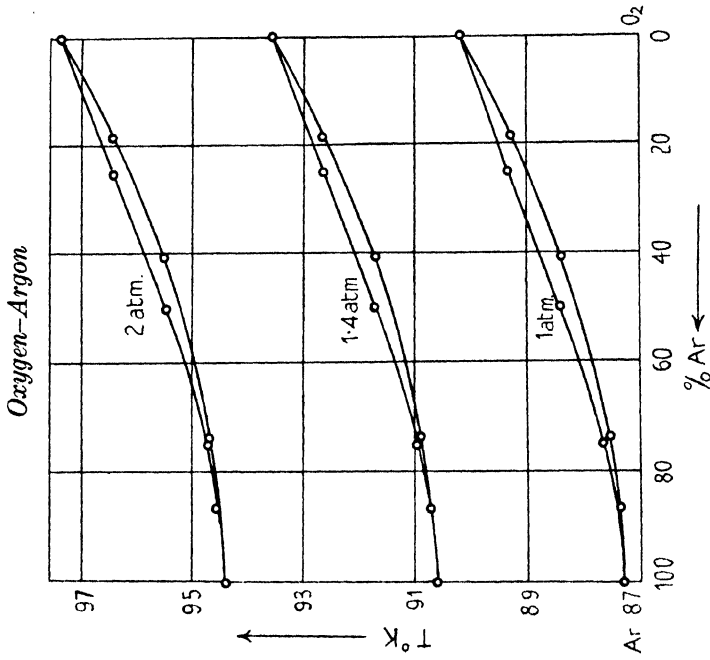


FIG. 32.  $(T, x)$  curves at 1, 1.4, and 2 atm. Bourbo and Ischkin, 'Boiling-point Method' (see Fig. 31)

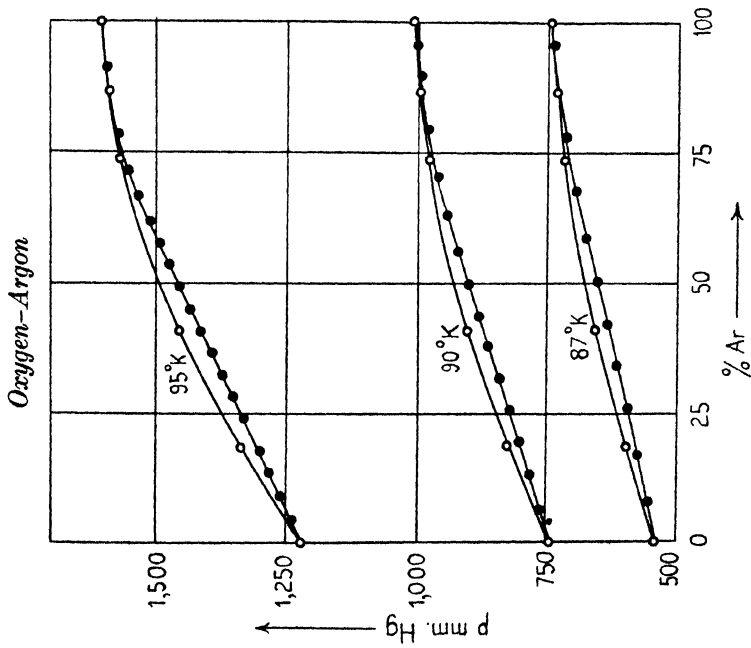


FIG. 31.  $(p, x)$  curves at 87, 90, and 95° K. Bourbo and Ischkin, 'Boiling-point Method', *Phys. Zeitschr. d. Sowjetunion*, 10, 271 (1936)

## Argon-Nitrogen

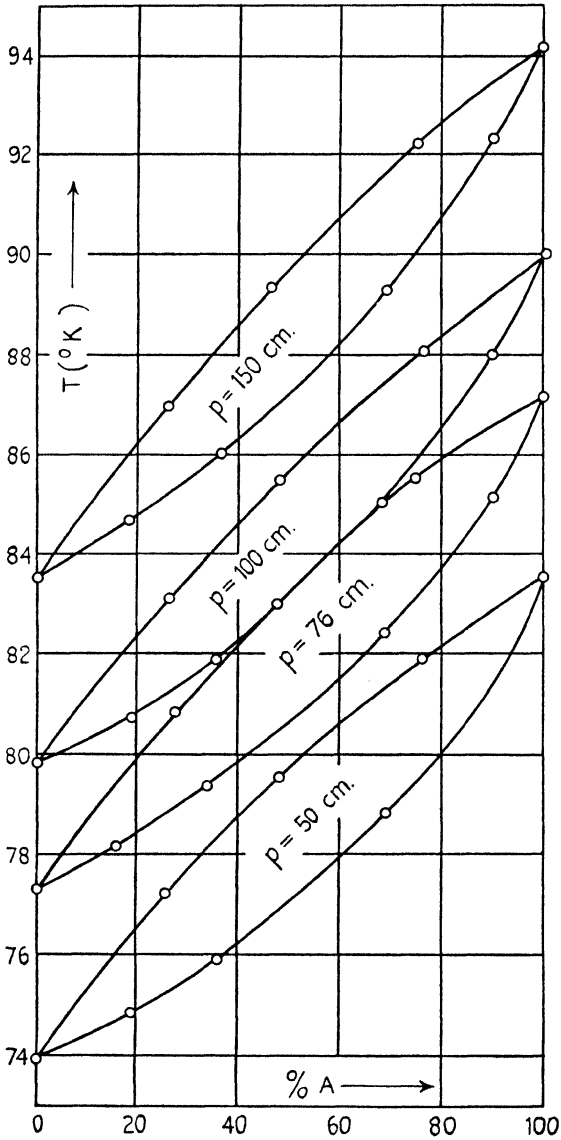


FIG. 33.  $(T, x)$  curves at 50, 76, 100, and 150 cm. Hg. Holst and Hamburger, 'Dew- and Boiling-point Method', *Zeitschr. f. phys. Chem.* **91**, 513 (1916)

## Carbon monoxide-Nitrogen

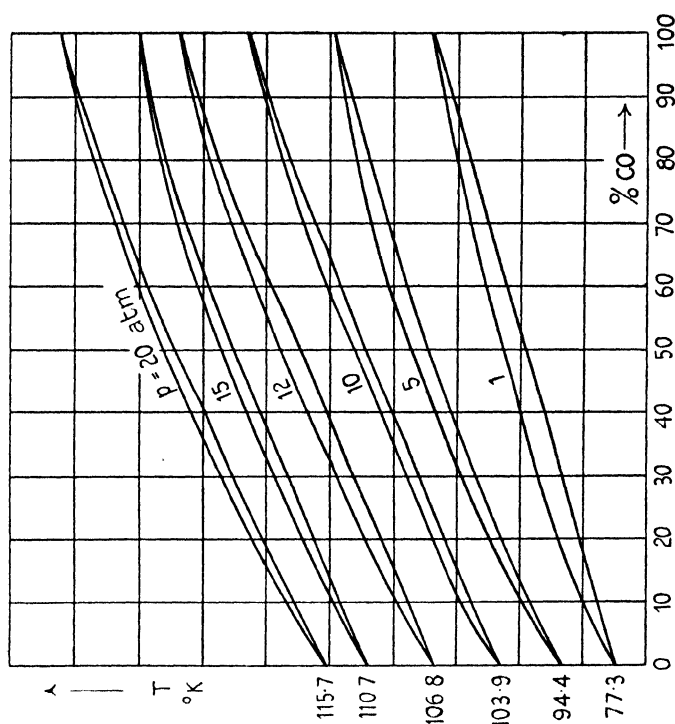


Fig. 35. ( $T, x$ ) curves at 1, 5, 10, 12, 15, and 20 atm. Yushkevich and Torochesnikov, 'Circulation Method', *Zhurn. khim. Prom.* 13, No. 21, p. 1273 (1936).

## Argon-Nitrogen

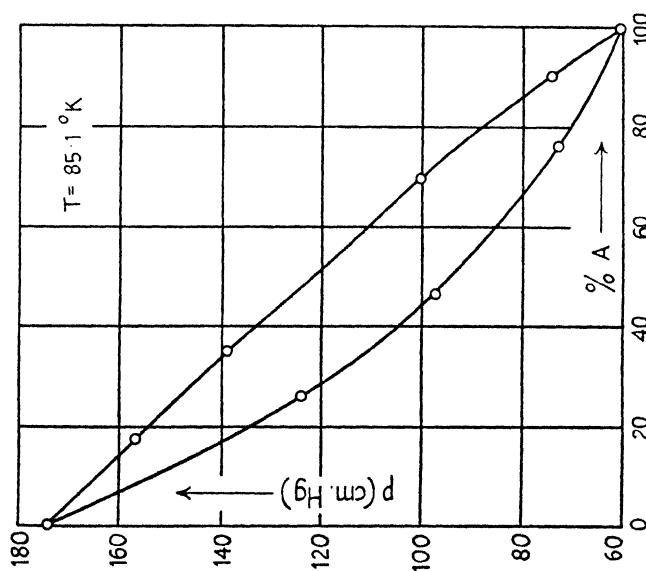


Fig. 34. ( $p, x$ ) curve at  $85^{\circ}\text{C}$ . Holst and Hamburger, 'Dew- and Boiling-point Method' (see Fig. 33)

## Carbon monoxide-Nitrogen

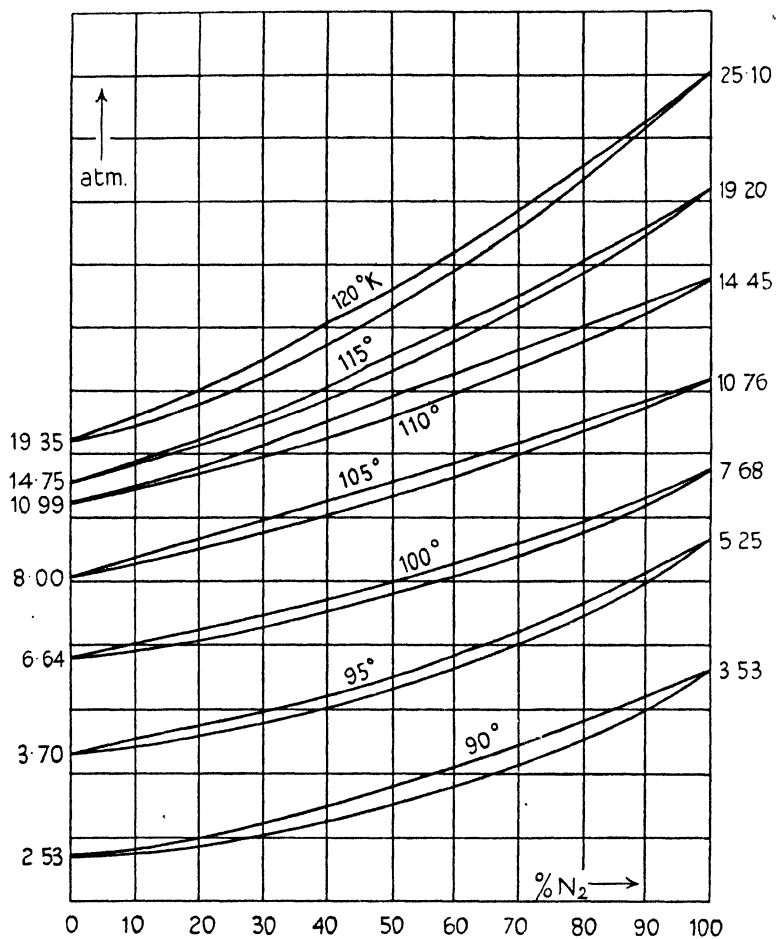


FIG. 36. ( $p, x$ ) curves at 90, 95, 100, 105, 110, 115, and 120° K. Yushkevich and Toroeshnikov, 'Circulation Method', *Zhurn. khim. Prom.* 13, No. 21, p. 1273 (1936)

## Nitrogen-Hydrogen

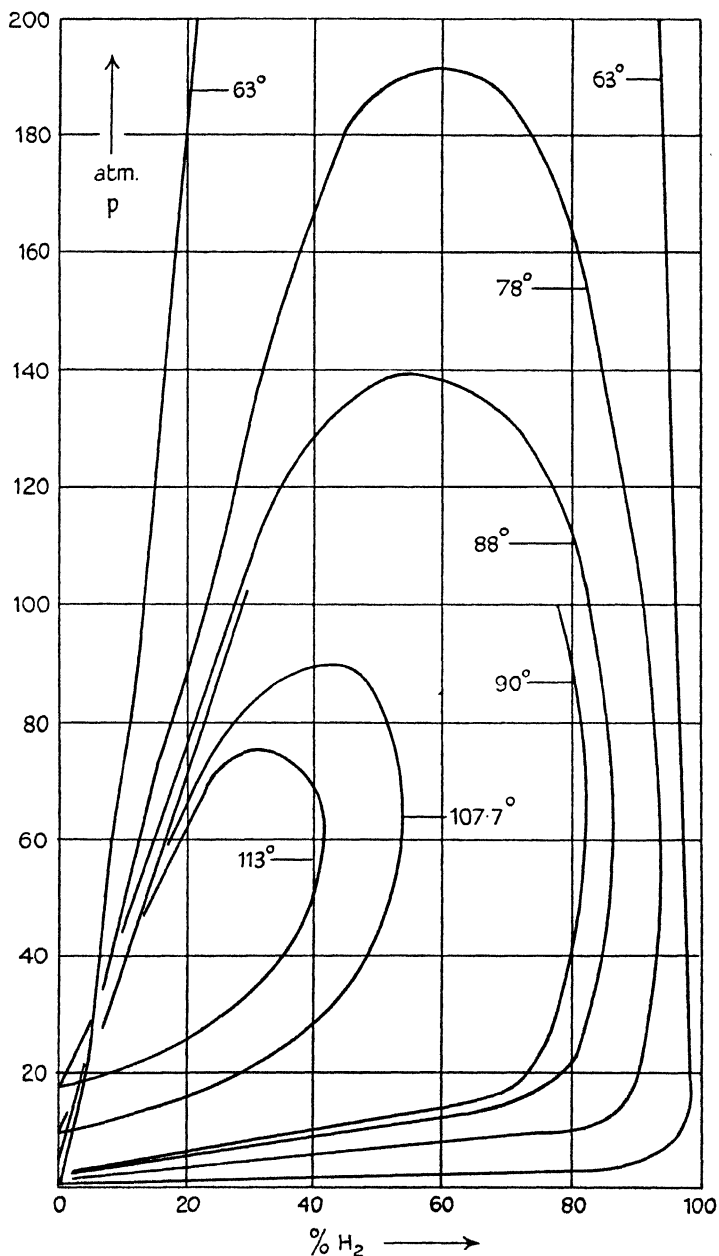


FIG. 37. ( $p, x$ ) curves at  $63, 78, 88, 90, 107.7$ , and  $113^\circ \text{K}$ . Verschoyle, 'Static Method', *Trans. Roy. Soc. (A)*, **230**, 189 (1931); Steckel and Zinn, 'Flow Method', *Zhurn. khim. prom.* **16**, No. 8 (1939); Ruhemann and Zinn, 'Flow Method', *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937)

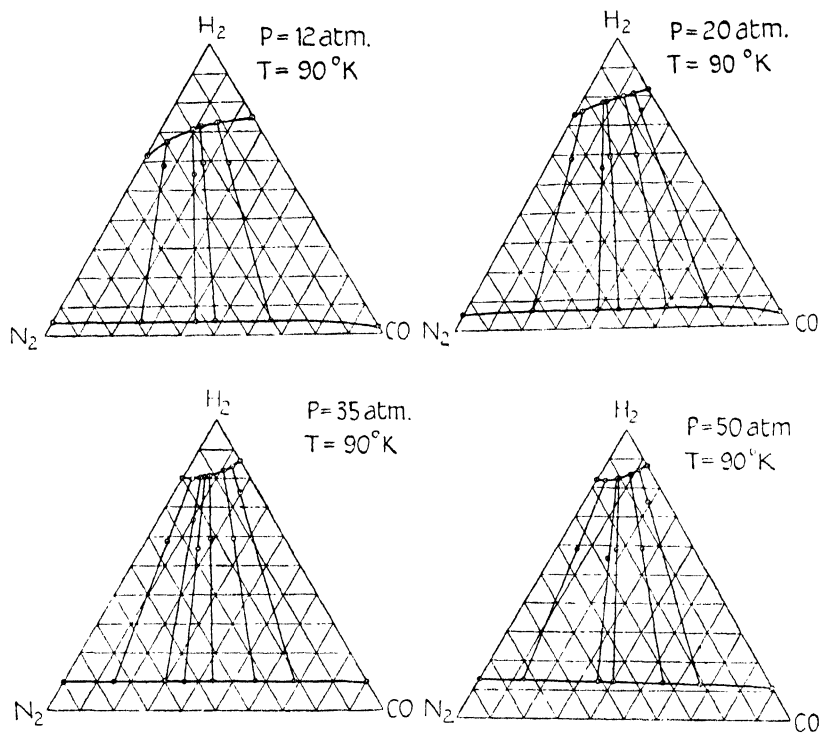
*Carbon monoxide-Nitrogen-Hydrogen*

FIG. 38. Equilibrium curves at 90° K. and at 12, 20, 35, and 50 atm. Ruhemann and Zinn, 'Flow Method' (see Fig. 37). Curves also obtained at lower temperatures

## Carbon monoxide-Hydrogen

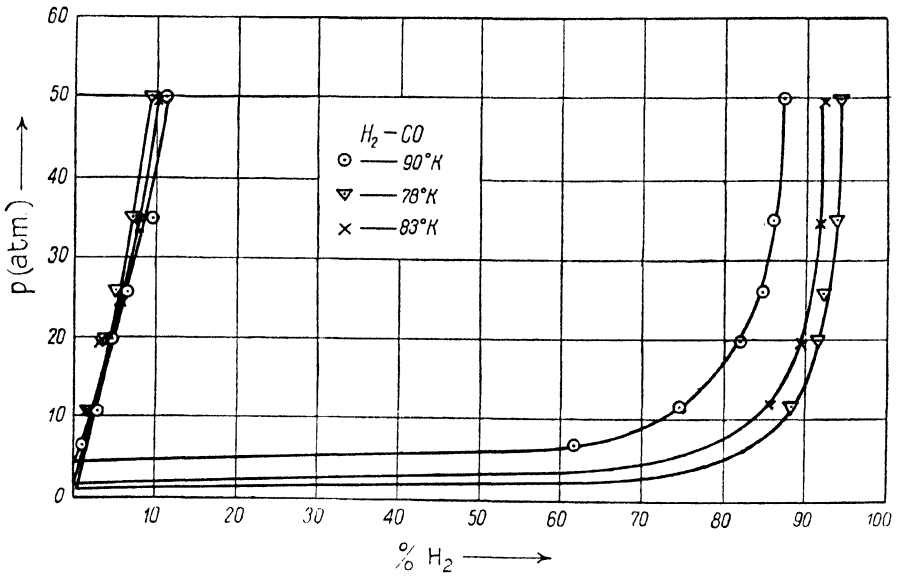


FIG. 39. ( $p, x$ ) curves at 78, 83, and  $90^\circ\text{K}$ . Ruhemann and Zinn, 'Flow Method', *Phys. Zeitschr. d. Sowjetunion*, **12**, 389 (1937)

## Methane-Hydrogen

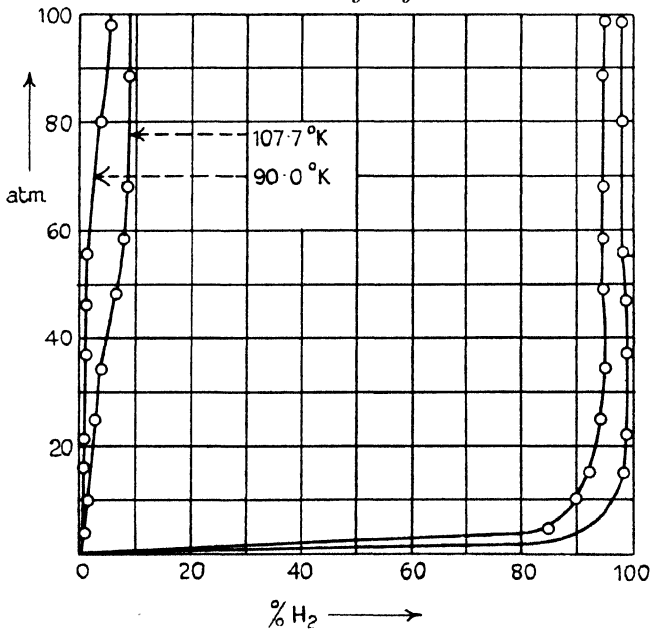


FIG. 40. Freeth and Verschöyle, 'Static Method', *Proc. Roy. Soc. (A)*, **130**, 453 (1931); Steckel and Zinn, 'Flow Method' (see Fig. 37)



# Methane-Nitrogen

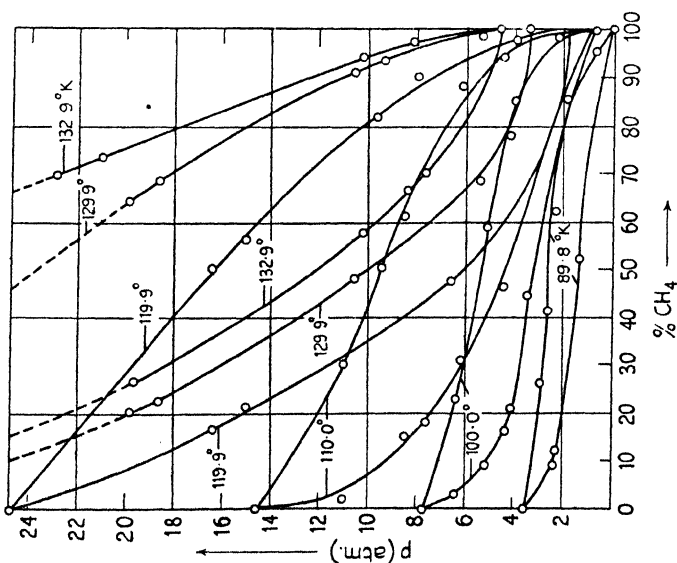


FIG. 41. (*p, x*) curves at 89.8, 100.0, 110.0, 119.9, 129.9, and 132.9° K. Torochesnikov and Levius, 'Circulation Method', *Zhurn. khim. prom.* **16**, No. 1, p. 19 (1939)

# Hydrogen-Nitrogen-Methane

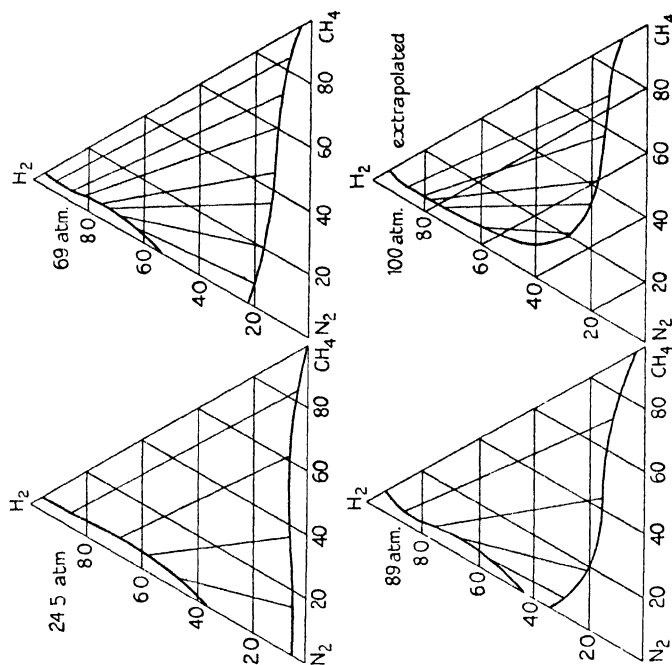


FIG. 42. Dew- and boiling-curves at 107.7° K., at 24.5, 69, and 89 atm., and at 100 atm. extrapolated. Steckel and Zimm, 'Flow Method', *Zhurn. khim. prom.* **16**, No. 8, p. 24 (1939). (The paper contains further curves at lower and intermediate pressures, as well as a series at 90° K.)

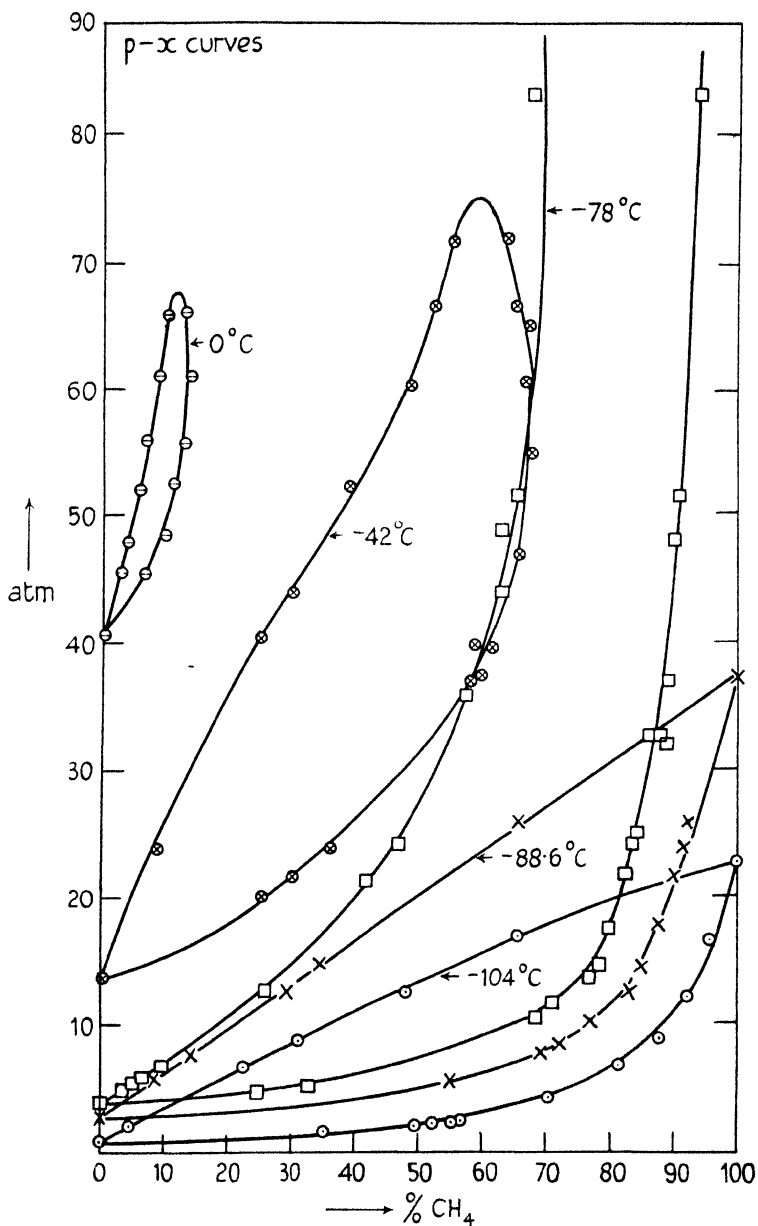
*Methane-Ethylene*

FIG. 43. ( $p, x$ ) curves at  $-104$ ,  $-88$ ,  $-78$ ,  $-42$ , and  $0^\circ\text{C}$ . Guter, Newitt, and Ruhemann, 'Flow Method', *Proc. Roy. Soc. (A)*. (In the press.) (In the upper part of the curves for  $-78^\circ$ , equilibrium was not attained. Later experiments show that the curves close at about 55 atm.)

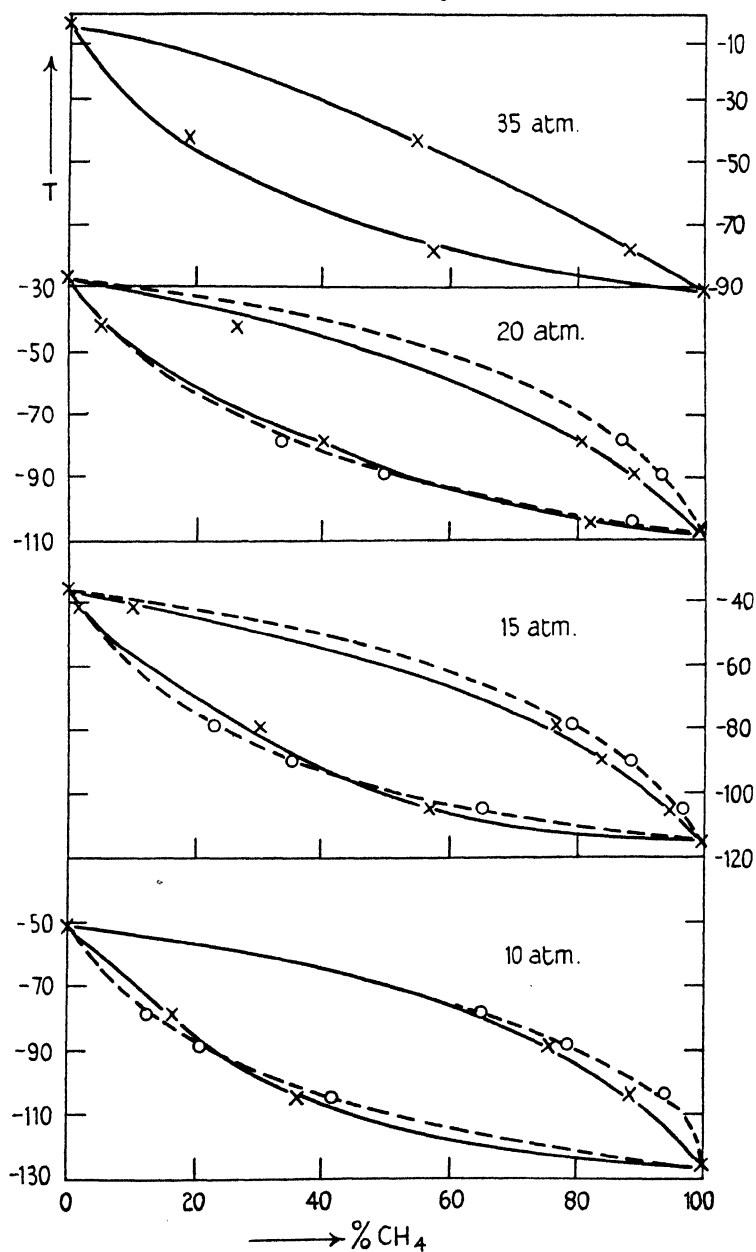
*Methane-Ethylene*

FIG. 44. ( $T, x$ ) curves at 10, 15, 20, and 35 atm. Guter, Newitt, and Ruhemann, 'Flow Method', *Proc. Roy. Soc. (A)*. (In the press.) (The dotted curves were calculated assuming the mixtures to be perfect solutions)

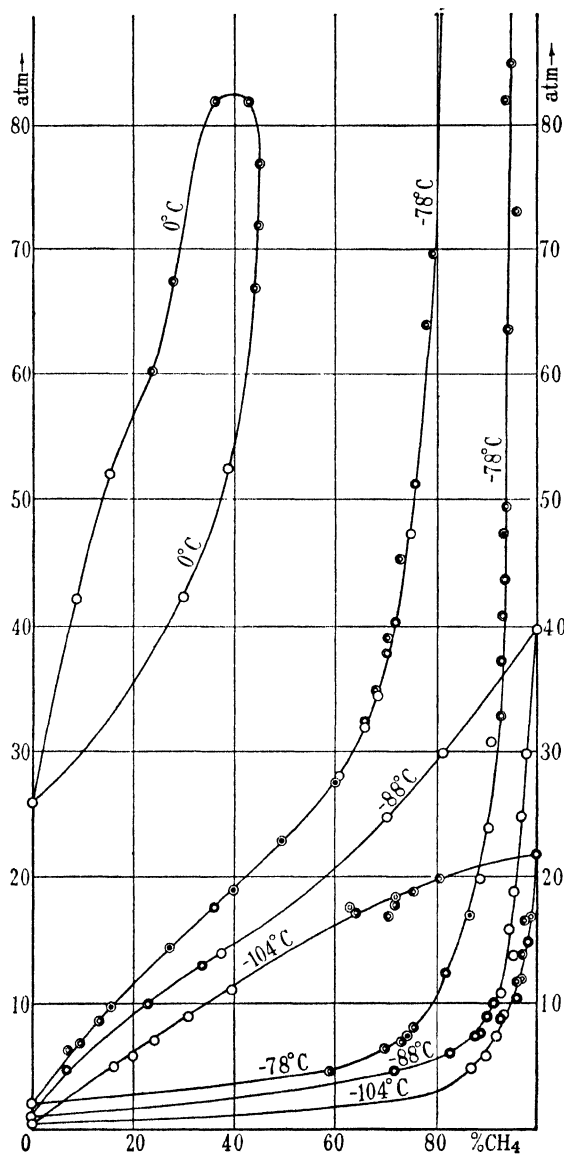
*Methane-Ethane*

FIG. 45. ( $P, x$ ) curves at  $-104$ ,  $-88$ ,  $-78$ , and  $0^\circ\text{C}$ . Ruhemann, 'Flow Method', *Proc. Roy. Soc. (A)*, **171**, 121 (1939). (In the upper part of the curves for  $-78^\circ$  equilibrium could not be attained. Later experiments show that the curve closes at about 60 atm.)

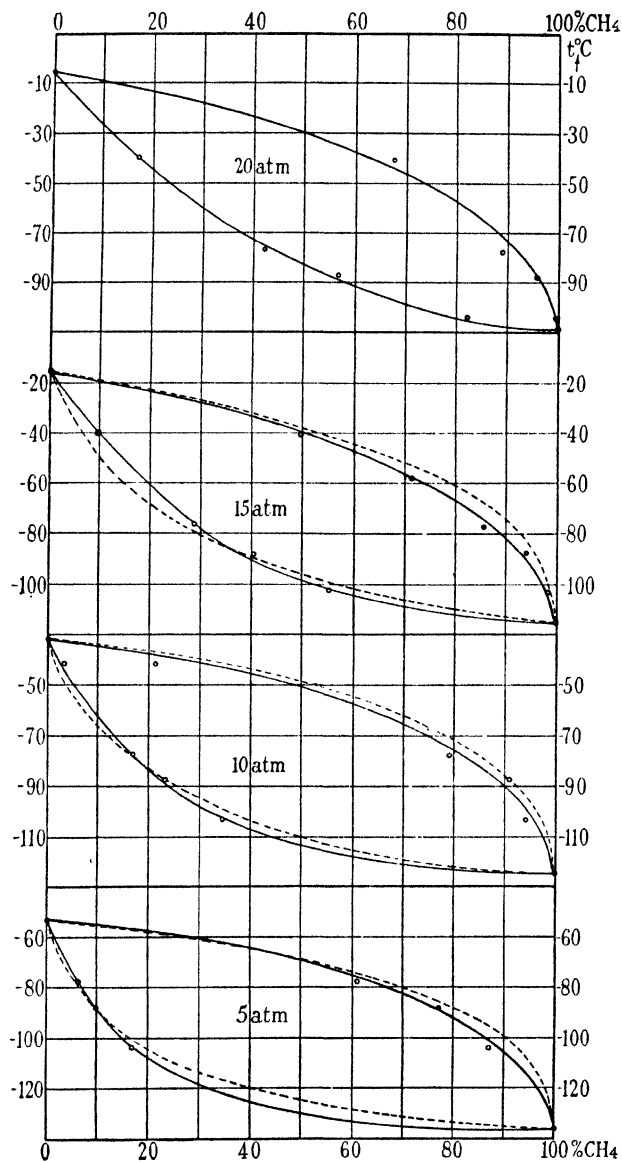
*Methane-Ethane*

FIG. 46. ( $T, x$ ) curves at 5, 10, 15, and 20 atm. Ruhemann, 'Flow Method', *Proc. Roy. Soc. (A)*, **171**, 121 (1939). (The dotted curves were calculated assuming the mixtures to be perfect solutions)

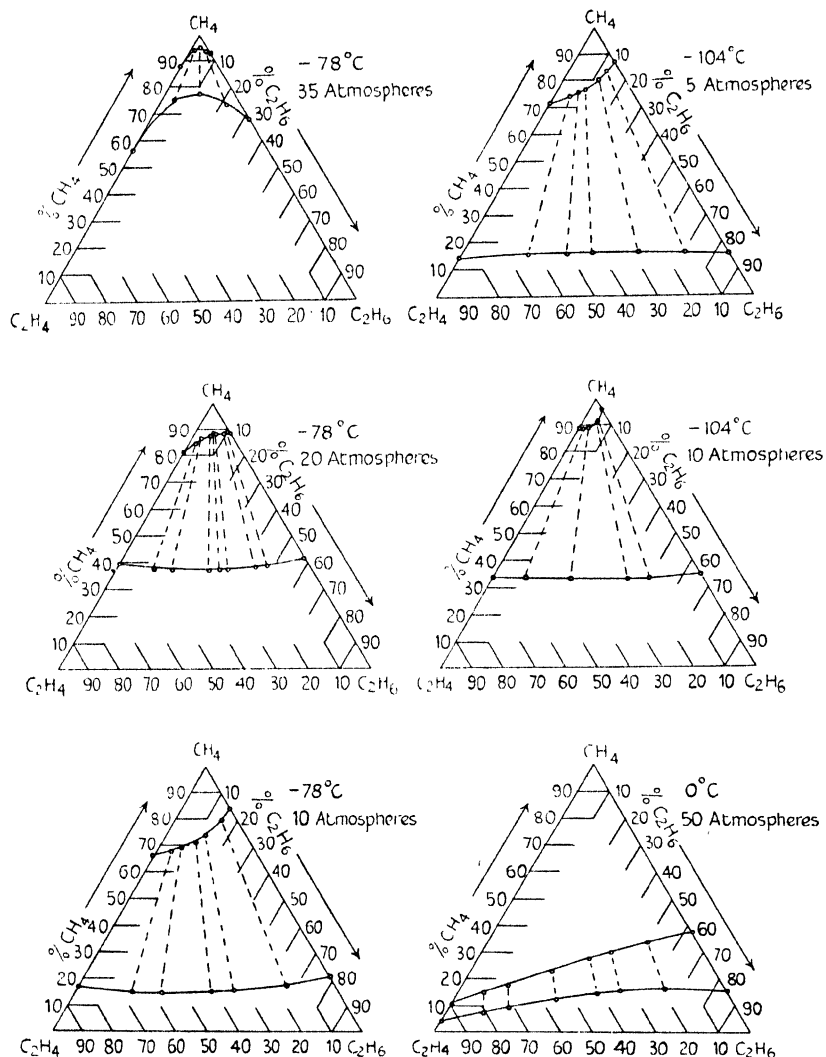
*Methane-Ethylene-Ethane*

FIG. 47. Dew- and boiling-curves at  $-104^\circ\text{C}$ . for 5 and 10 atm., at  $-78^\circ\text{C}$ . for 10, 20, and 35 atm., and at  $0^\circ\text{C}$ . for 50 atm. Guter, Newitt, and Ruhemann, 'Flow Method', *Proc. Roy. Soc. (A)*. (In the press.)

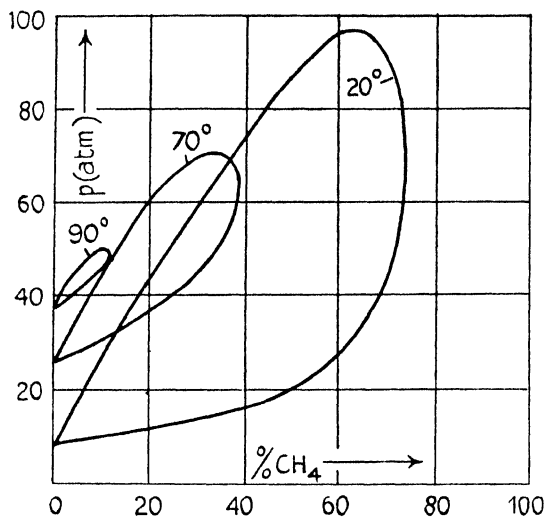
*Methane-Propane*

FIG. 48. ( $p, x$ ) curves at 20, 70, and 90° C. Sage, Lacey, and Schaafsma, 'Dew- and Boiling-point Method', *Ind. Eng. Chem.* **26**, 214 (1934)

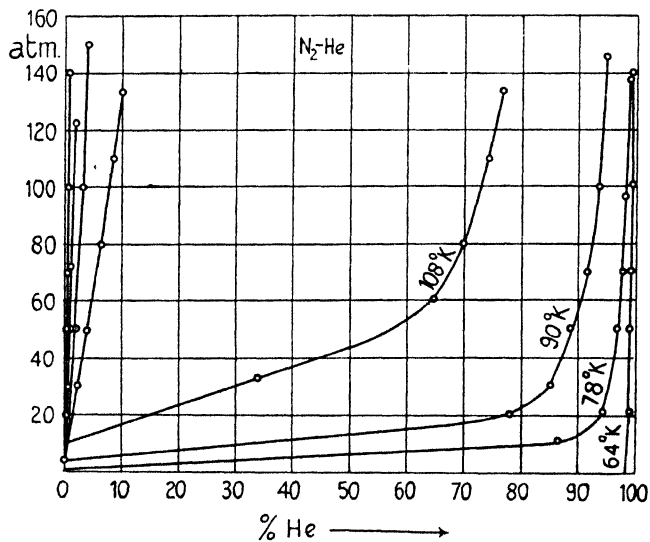
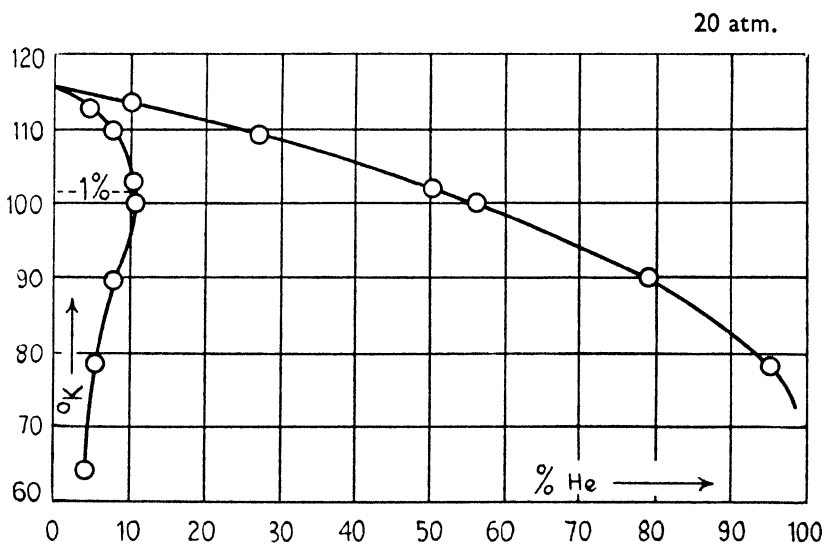
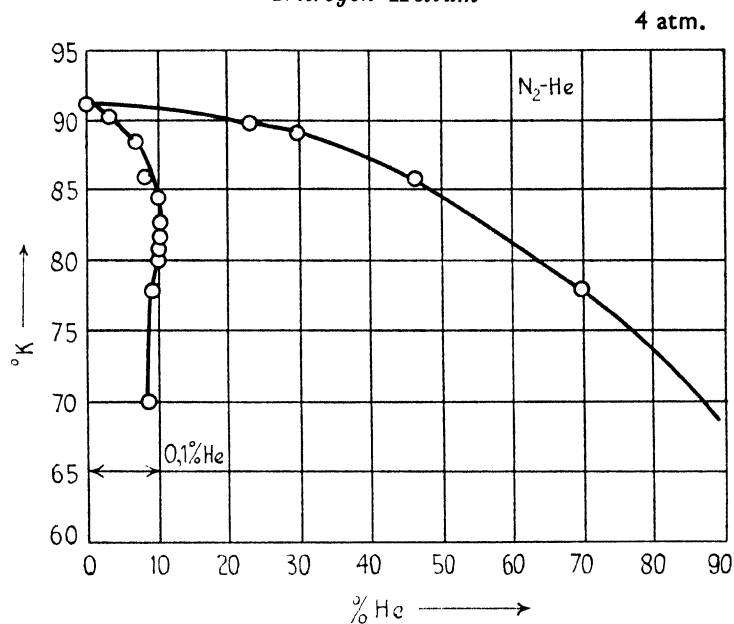
*Nitrogen-Helium*

FIG. 49. ( $p, x$ ) curves at 64, 78, 90, and 108° K. Fedoritenko and Ruhemann, 'Static and Flow Methods', *Techn. Phys. of the U.S.S.R.* **4**, 1 (1937)

## Nitrogen-Helium



FIGS. 50 AND 51.  $(T, x)$  curves at 4 and 20 atm. Fedoritenko and Ruhemann, 'Static and Flow Methods', *Techn. Phys. of the U.S.S.R.* **4**, 1 (1937). The composition scale for the boiling curves has been magnified as indicated.



### III

## THE METHODS OF GAS SEPARATION

### 1. Condensation and evaporation

CONSIDER a mixture containing 80 per cent. nitrogen and 20 per cent. helium at 20 atm. pressure to be cooled gradually below its point of liquefaction. To see what happens, let us turn to the  $(T, x)$  diagram of this mixture in Fig. 51. We note that liquefaction begins at  $110.5^\circ \text{K.}$  and that the liquid first condensed contains 99.3 per cent. nitrogen. Thus, even the first drop of condensed liquid is almost pure nitrogen. However, the gaseous phase still contains only 20 per cent. helium. If we now cool the mixture further, we enter the inhomogeneous region. At  $108^\circ$  the liquid is slightly impurer, 99.1 per cent.  $\text{N}_2$ , but the gas already contains 30 per cent. He. By applying the lever rule along the connodal for  $108^\circ$ , we find that 37 per cent. of the mixture has been condensed. By lowering the temperature still further, we obtain the figures of Table 8, which show us how the separation proceeds when more and more gas is condensed.

Table 8 shows that by simply cooling the mixture of 80 per cent. nitrogen and 20 per cent. helium to  $77^\circ \text{K.}$ , we can separate it into 99.6 per cent. liquid nitrogen and 98 per cent. gaseous helium. For most technical purposes the purity of these products will be sufficient. By lowering the temperature still further, a yet higher degree of purity might be obtained. It is interesting to observe that the amount of helium dissolved in liquid nitrogen at first increases as the temperature is lowered and passes through a maximum at about  $101^\circ \text{K.}$

TABLE 8. *Separation of a Helium-Nitrogen Mixture by Simple Condensation at 20 atm. Composition of Mixture: 80 per cent.  $\text{N}_2$ , 20 per cent. He*

$T$	$x_{\text{N}_2}$	$z_{\text{He}}$	$\epsilon$
110.5	99.3	20	0
108	99.1	30	0.37
105	99.0	40	0.54
101	99.0	50	0.64
98	99.1	60	0.69
93.5	99.2	70	0.74
89	99.3	80	0.77
82.5	99.4	90	0.79
77	99.6	98	0.80

$x_{\text{N}_2}$  = mole per cent. nitrogen in liquid;  $z_{\text{He}}$  = per cent. helium in gas;  $\epsilon$  = fraction of mixture condensed.

As a further example let us take atmospheric air, which may here be considered as consisting of 79 per cent.  $N_2$  and 21 per cent.  $O_2$ , the other components being neglected. Suppose the air to be cooled at a constant pressure of 1 atm., and let us follow the process of condensation on the  $(T, x)$  diagram of Fig. 30. The equilibrium concentrations are here given by the ends of the horizontal connodals on the dew- and boiling-curve. The results are listed in Table 9.

From Table 9 it is evident that simple condensation will never lead to anything like a complete separation of oxygen and nitrogen. As the temperature falls through the inhomogeneous region, the oxygen concentration decreases simultaneously in both phases. When the boiling-point is reached, the last bubble of vapour to condense contains 93.5 per cent.  $N_2$ , but in the meantime so much nitrogen has condensed that the liquid phase now has the same composition as the original gas. Simple condensation of oxygen-nitrogen mixtures produces only small changes in the relative concentrations of the liquid and gaseous phases.

TABLE 9. *Simple Condensation of Atmospheric Air at 1 atm.*

$T$	$x_{O_2}$	$z_{O_2}$	$\epsilon$
81.4	49	21	0
81.0	46	17	0.12
80.0	35	13	0.37
79.0	24	8	0.80
78.8	21	6.5	1.00

From what we have said concerning simple condensation, we may easily infer that the evaporation of a liquid, like the condensation of a vapour, may or may not lead to the separation of the components, the result depending on the shape of the equilibrium curves. The direction in which the change of phase is carried out is of subsidiary importance.

In considering the change of composition occurring during the evaporation of a liquid mixture, we must, however, distinguish between two possible conditions under which the evaporation may take place. The process may be conducted in such a way that the vapour formed remains in contact with the liquid throughout. On the other hand, it is more usual in practice to withdraw the vapour from the liquid as it is formed. In the first case, which is known as *closed evaporation*, at every stage of the process the whole of the vapour is, at any rate approximately, in equilibrium with the remaining liquid. In the second case, known as *open evaporation*, only the small amount of vapour just

formed is in equilibrium with the liquid residue; the rest of the vapour, which has been withdrawn, no longer interacts with the liquid at all.

Let us consider the case of closed evaporation first. Let  $m_0$  be the initial amount of liquid, and  $x_0$  the concentration of the more volatile component. After an amount  $M$  has evaporated, let  $m$  be the amount

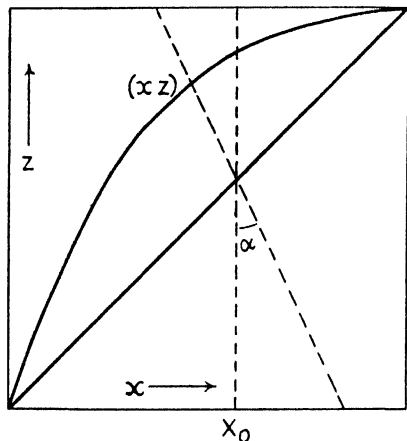


FIG. 52. Construction to determine change of composition during 'closed' evaporation

of liquid left over and  $x$  its composition. The concentration of the more volatile component in the vapour will then be  $z$ , and vapour and liquid will be in equilibrium. Since the amount of the more volatile component in both phases together remains the same throughout the process,

$$mx + Mz = (m + M)x_0.$$

Therefore

$$M/m = (x_0 - x)/(z - x_0).$$

This is merely the lever rule over again.

To determine  $x$  and  $z$ , when  $m$ ,  $M$ , and  $m_0$  are known, consider Fig. 52, in which  $z$  is shown as a function of  $x$ . From a point on the diagonal the abscissa of which is  $x_0$  draw a straight line sloping upwards from right to left at an angle  $\alpha = \tan^{-1} M/m$  with the vertical. This line intersects the  $z$ -curve at the point  $(x, z)$ .† In the special case of perfect solutions  $x$  and  $z$  can be computed analytically.

Now suppose the evaporation to be 'open'. When a small amount  $dM$  evaporates, the composition of the liquid will change from  $x$  to  $x + dx$ , and the amount of liquid will change by  $dm = -dM$ . With the same considerations as before we obtain

$$mx - (m + dm)(x + dx) = z dM = -z dm,$$

whence, neglecting the product  $dmdx$ ,

$$dm/m = dx/(z - x),$$

or

$$\log m/m_0 = \int_{x_0}^x dx/(z - x).$$

† See Hausen, 'Materialtrennung durch Destillation und Rektifikation', *Der Chemie-Ingenieur*, I, part 3, ch. xv, §13, p. 100. Leipzig, 1933.

This equation cannot, in general, be integrated except for a perfect solution with constant  $\epsilon$ . It can, however, be integrated graphically in small steps as follows. Let a small amount  $\Delta M$  evaporate. The amount of liquid will change from  $m_1$  to  $m_2 = m_1 - \Delta M$ , and its composition from  $x_1$  to  $x_2$ . The composition of the vapour will lie between

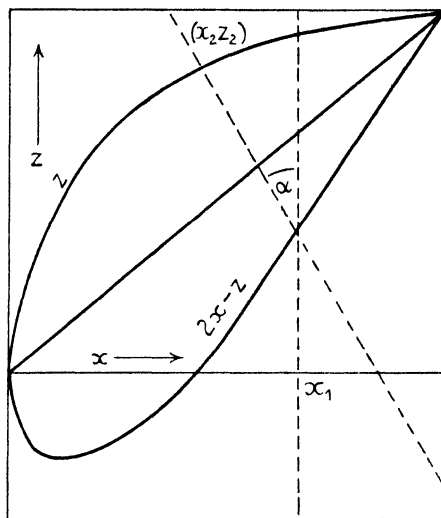


FIG. 53. Construction to determine change of composition during 'open' evaporation

$z_1$  and  $z_2$ ,  $z_1$  being in equilibrium with  $x_1$ , and  $z_2$  with  $x_2$ . If  $\Delta M$  is sufficiently small we can put  $z = \frac{1}{2}(z_1 + z_2)$ . We then obtain

$$M \frac{1}{2}(z_1 + z_2) + m_2 x_2 = (m_2 + \Delta M)x;$$

whence

$$x_1 - x_2 = \frac{\Delta M}{2m_2} [z_2 - (2x_1 - z_1)].$$

In Fig. 53, in addition to  $z$ , the curve  $2x - z$  has been drawn as a function of  $x$ . This curve is easily obtained, as it is everywhere the same distance below the diagonal as  $z$  is above it. If we now draw a straight line through a point on the curve  $2x - z$  with abscissa  $x_1$  at an angle  $\alpha = \tan^{-1} \Delta M / 2m_2$ , it will intersect the curve  $z$  at the point  $(x_2, z_2)$ .

Figs. 54 and 55 show the course of closed and open evaporation of a perfect binary mixture with  $\epsilon = 4$  (see equation (34), Ch. II) with an initial concentration of 80 per cent. of the more volatile component. The behaviour is similar to that of air. It will be seen that open evaporation enables the less volatile component to be obtained in a pure state, but with an infinitely small yield.

Though condensation and evaporation are in themselves frequently insufficient to separate a mixture into its component parts, yet they feature to a large extent in all separating apparatus, since it is through

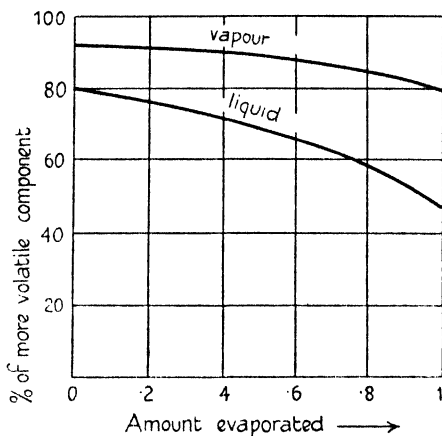


FIG. 54. Closed evaporation of a perfect mixture containing 80 per cent. of more volatile component.  $\epsilon = 4$

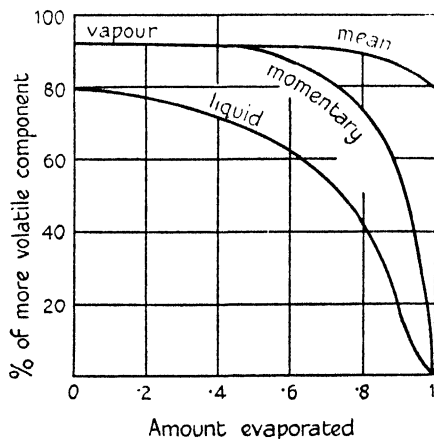


FIG. 55. Open evaporation of a perfect mixture containing 80 per cent. of more volatile component.  $\epsilon = 4$

them that the two-phase equilibrium is brought about, which is at the basis of all separating processes. There are two fundamental methods of effecting a transition from a gaseous to a liquid phase and vice versa. One consists in altering the pressure of the substance in such a way as to intersect an equilibrium curve. This will be treated in some detail

in Chapter V, when we discuss refrigeration and liquefaction. The other way to bring about condensation or evaporation is by a direct transfer of heat from or to the substance, while the pressure remains unchanged. This can be effected only if we have at our disposal in sufficient quantities a substance which is warmer or colder than the substance treated. If this substance is colder than that treated, it is known as a refrigerant. In this case the transfer of heat to the refrigerant may lead to the condensation of the working substance. The 'new' substance need not be different from the one that is being treated. It may be the same substance at a different temperature, it may be a mixture containing the same components as the working substance, but with different concentrations; in short, it may be the mixture treated at a different stage of separation. On the other hand, it may be quite a different substance, the only object of which is to transfer heat to or from the mixture that is being separated. It may be divided from the latter by metallic walls, in which case only heat will be transferred; it may, however, be brought into direct contact with the mixture. In this case a transfer of matter will take place as well as a transfer of heat.

In every case the transfer of heat from one substance to another calls for a difference in temperature between the two. Only if such a temperature head exists, will heat actually pass from one to the other. Indeed, other things being equal, the amount of heat that will flow in a given time across a given surface is directly proportional to this temperature head. On the other hand, as we shall see in Chapter IV, the direct transfer of heat between two substances at different temperatures is an irreversible process and as such entails the expenditure of additional work. Whereas from the point of view of securing a rapid transfer of heat it is profitable to maintain a large temperature head between the two substances, from the point of view of power economy this temperature head should be kept as small as possible. Clearly some compromise must be reached between these two extremes.

We shall here consider condensation and evaporation due to heat transfer through metal walls, in which only heat flows and no matter.

1. Partial condensation of a vapour can be brought about by bringing it into thermal contact with a gas at a lower temperature. This is generally done with the help of a counter-current heat-exchanger. The vapour to be condensed is passed through a pipe which contains a large number of narrow tubes traversed by the cold gas (see Fig. 56). Part of the vapour in the pipe condenses on the walls of the tubes and the latent heat of condensation is absorbed by the gas. Sometimes the pipe

contains baffles to increase the path of the vapour. Sometimes the vapour to be condensed is passed through the narrow tubes and the gaseous refrigerant flows through the wider tube.

This method is usually restricted to the condensation of small quantities of vapour, such as small impurities with higher boiling-points

than the bulk of the gas. For the heat capacities of gases per unit volume are comparatively small, except at very high pressures, in view of their low density, and therefore large quantities of heat are difficult to absorb in them. Since latent heats of condensation are large compared with the specific heats of gases, the condensation of large quantities of vapour would necessitate very large temperature heads at one end of the apparatus.

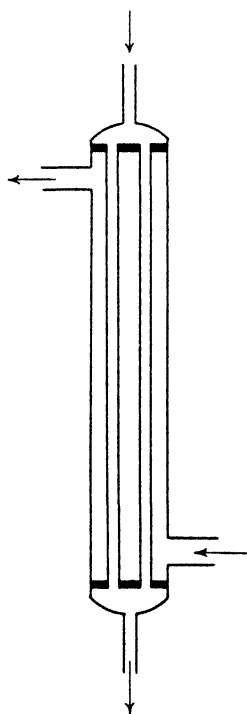


FIG. 56. Condenser-exchanger

2. Large quantities of liquid are frequently evaporated by immersing in them tubes traversed by warm gases, more especially at high pressures, above the critical pressure of the gas. Though no change of phase occurs in the gas at these pressures, its specific heat is frequently high enough to allow of large quantities of heat being transferred. But here, too, the temperature head between the ingoing gas and the evaporating liquid must be considerable. In the case of some gas separators temperature heads of more than  $100^{\circ}\text{C}$ . occur in the evaporators. The high-pressure gas in the tubing may be cooled almost to the

temperature of the liquid, so that the temperature head at the outlet may be quite small; it is usually about  $3\text{--}4^{\circ}\text{C}$ . Frequently the high-pressure gas is the same mixture as that evaporating, with slightly different concentrations. After being cooled in the tubing almost to the temperature of the liquid, it is expanded in a valve, thereby partially liquefied and delivered to the apparatus (see Fig. 57). The liquefied portion, possibly after undergoing some further process of separation, collects in the evaporator, where it is kept boiling by the passage of fresh, warm gas.

3. By far the most important method of condensing a vapour and evaporating a liquid is to combine the two processes by allowing the liquid to evaporate at the expense of the latent heat of condensation

of the vapour. A frequent type of condenser-evaporator is depicted in Fig. 58. It consists of a large number of parallel, narrow copper tubes, held together by perforated plates at top and bottom, as in the heat-exchanger type described under (1). Often several hundreds, or even thousands, of tubes are used. Above the condenser is a copper dome with an exit for the uncondensed vapour. The mixture to be condensed

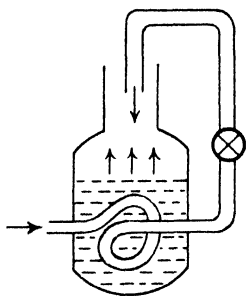


FIG. 57. Evaporator

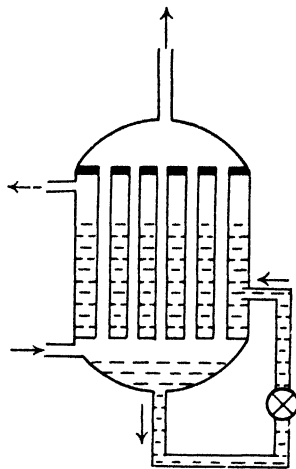


FIG. 58. Condenser-evaporator

is introduced into the tubes from below. The liquid flows continuously into the space between the tubes and evaporates as the mixture in the tubes condenses.

Here, as before, the evaporating liquid must be colder than the condensing vapour in order that the latent heat may be transferred from one to the other. Again the liquid may be a 'foreign' refrigerant, or it may be the same mixture as that condensing, at a different stage of the process. Frequently, when the condensing vapour is at a pressure above atmospheric, the liquid so formed will be expanded outside the condenser and delivered back as a refrigerant (see Fig. 58).

An example of this type of condenser-evaporator, fed with a foreign refrigerant, is found in the condensation of methane from coke-oven gas in the production of hydrogen-nitrogen mixtures for ammonia synthesis. In this case the refrigerant is liquid nitrogen supplied from a special cycle. The process will be discussed in detail in Chapter X. In air separation (see Chapter VI) a similar arrangement is used to condense liquid nitrogen under pressure with the help of liquid oxygen boiling at atmospheric pressure. Here the condensing vapour and the refrigerant are part of the same air which is being separated.



## 2. Dephlegmation

Consider the condenser-evaporator depicted in Fig. 58, and suppose that the vapour condensing in the tubes and the liquid boiling between the tubes are one and the same binary mixture. As we have seen, a mixture condenses in a finite temperature interval and the composition of the liquid formed varies as the condensation proceeds. A temperature head will therefore tend to be set up between the top and bottom of the apparatus inside the tubes in which the vapour is condensing. The temperature at the bottom of the tubes will correspond roughly to that of the commencement of condensation, and the temperature at the top will be lower. Simultaneously, there should be a difference in composition in respect to each phase between the top and the bottom.

Consider a certain section of a condenser, through the tubes of which a mixture of oxygen and nitrogen is passing at 5 atm. Suppose the initial composition of the mixture on entering the condenser from below was 50 per cent.  $N_2$  and 50 per cent.  $O_2$ . If the temperature of the liquid between the tubes is sufficiently low, a certain amount of the mixture will have condensed by the time it has reached the section. If, say, one-third has condensed, we may infer from the equilibrium diagram of Fig. 30 that the gaseous phase will contain about 43 per cent.  $O_2$  and the liquid some 67 per cent.  $O_2$ . But the liquid, owing to its greater specific gravity, will for the most part drip downwards along the walls of the tubes and never reach the higher sections of the condenser. Now, if the walls of the tube are cold enough, the vapour, as it rises above the section, will continue to condense. It will, in fact, behave just as the original vapour of 50 per cent.  $O_2$  behaved, only now it will contain only 43 per cent.  $O_2$ . Suppose that when it has reached a higher section another third has condensed. From the  $(T, x)$  diagram we may conclude that the gas will now contain 35 per cent.  $O_2$ . Apparently, if the condenser is long enough and the liquid between the tubes cold enough, this process can be carried on indefinitely.

The numerical data that we have just given are obviously rough and our arguments at the best approximate. All they really show is that the vapour in the upper part of the condenser will contain less oxygen than that condensed at the bottom. Actually we shall have a current of comparatively warm gas moving upwards and a stream of cold liquid trickling downwards along the walls of the tubes. The vapour will interact not with the walls directly but with the layer of liquid trickling down them. This liquid will contain more oxygen than the gas with

which it interacts but less oxygen than a liquid should contain that is in equilibrium with the vapour interacting with it. Part of the gas will condense, the liquid formed containing more oxygen than the vapour itself, and part of the liquid will evaporate, the vapour formed containing less oxygen than the liquid. As a result, the liquid trickling down the tubes will gradually become enriched with oxygen as it moves downwards, and the vapour will simultaneously become enriched with nitrogen on its way up the condenser. The liquid escaping from the bottom of the condenser cannot contain more oxygen than is in equilibrium with the gaseous mixture entering the tubes, but if the condenser is long enough and the refrigerating liquid cold enough, the vapour emerging at the top of the condenser may come to be almost pure nitrogen.

This procedure, which was first applied in low-temperature gas separation by Claude, is called *dephlegmation*, and a condenser so constructed as to enhance this effect as much as possible is termed a *dephlegmator*. The liquid formed in a dephlegmator and emitted downwards through the tubes is known as *reflux*.

Now consider a dephlegmator of the type shown in Fig. 59*a*, and suppose that the mixture entering at *A* is atmospheric air, precooled to the temperature at which condensation commences at the working pressure. We shall leave this pressure undetermined for the time being. We have seen that the vapour emerging at *E* can be almost pure nitrogen, and we shall suppose for the moment that the nitrogen is really pure. The liquid collecting at *B* may at the best have a composition corresponding to that of a liquid in equilibrium with atmospheric air at the working pressure. Actually it will contain a little more nitrogen. Suppose that we maintain 55 per cent. nitrogen at this point, a figure always obtainable. Within the tubes a temperature head will be set up, corresponding to the difference in the boiling-points of pure nitrogen and the liquid mixture formed at *B*.

Suppose that this liquid is expanded in the valve *V* to atmospheric pressure and delivered between the tubes of the condenser. Part will evaporate during the expansion, the rest as a result of condensation inside the tubes. Finally, all the liquid formed at *B* will emerge at *D* as a saturated vapour. The vapour leaving at *D* will, therefore, have the same composition as the liquid at *B*, i.e. 55 per cent. nitrogen. But in the stationary state the liquid boiling between the tubes will contain more oxygen than the vapour emitted at *D*. Its composition will, in fact, be that of a liquid in equilibrium with this vapour, namely, 22 per

cent. nitrogen. And since the vapour from this boiling liquid is ejected at *D* immediately it leaves the surface of the liquid, the composition of the liquid will be practically the same throughout. Its temperature will, therefore, also be the same throughout. This temperature will be  $85.3^{\circ}\text{K.}$ , the boiling-point, at atmospheric pressure, of a liquid con-

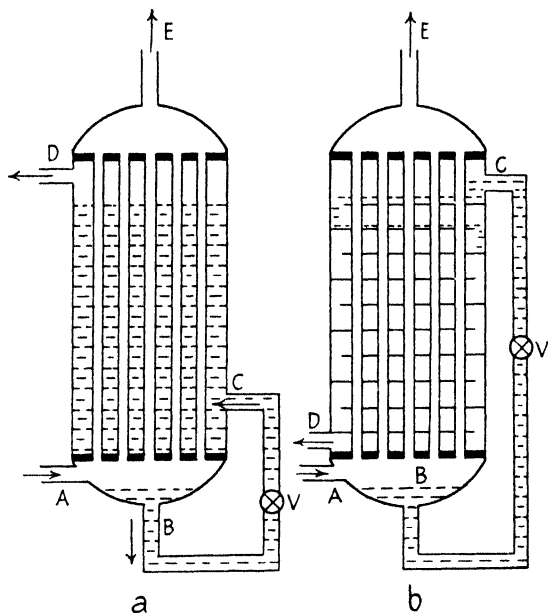


FIG. 59. Dephlegmators. *a* normal type, *b* with trays

taining 22 per cent. nitrogen. Outside the tubes there will be no appreciable temperature head between the top and bottom of the dephlegmator.

In order that heat may be transferred from the condensing vapour inside the tubes to the liquid boiling outside, the latter must be colder than the former. We shall assume that the surface of heat transfer is such as to require a temperature head of  $4^{\circ}\text{C.}$  between the inside and outside of the tubes, in order that the necessary quantity of heat may be transferred. Since the temperature inside the tubes varies with the height, this means that the temperature of the liquid outside must be  $4^{\circ}$  lower than that of the vapour condensing at the top, i.e. at the coldest point inside the tubes. But we have assumed that this vapour is pure nitrogen. So the temperature of the nitrogen must be  $85.3 + 4 = 89.3^{\circ}\text{K.}$  The vapour pressure of nitrogen boiling at  $89.3^{\circ}\text{K.}$  is 3.3 atm. abs. This is therefore the pressure that must be maintained

inside the tubes. To keep the process going, all the air must be compressed to 3.3 atm. This pressure determines the power consumption necessary to keep the plant working. It is therefore of importance to have the pressure as low as possible.

Now the temperature in the tubes at the bottom of the dephlegmator is the boiling-point, at 3.3 atm., of a mixture containing 55 per cent. nitrogen. This is  $93.5^{\circ}\text{K}$ . So the temperature head between condensing vapour and boiling liquid at the bottom of the apparatus is  $93.5 - 85.3 = 8.2^{\circ}\text{C}$ . This temperature head is unnecessarily high. It gives us more than we require and we may conceivably think that a more suitable construction of the dephlegmator might reduce the pressure needed to keep it working.

The fact that this type of dephlegmator gives rise to a temperature head between top and bottom inside the tubes, but not to a corresponding temperature head outside, is an important drawback, which we can best gauge by studying the effect of its elimination. Fig. 59*b* shows a dephlegmator of a new type, developed by Claude. The space between the tubes contains a series of horizontal trays, each with an aperture at the side. The liquid mixture that collects at *B* is admitted, after expansion, to the topmost tray at *C*. It trickles down from one tray to the next, evaporating all the time. Finally, when all has evaporated, the vapour emerges at *D* at the bottom of the apparatus.

In this case the vapour remains in contact with the liquid throughout the extent of the dephlegmator. The result of this is that the concentration of liquid and vapour varies from tray to tray. In our example the liquid at the top contains 55 per cent. nitrogen, and only the last drops of liquid, evaporating from the lowest tray, contain 22 per cent. nitrogen. For the same reason the temperature in the space between the tubes also varies with the height, from the boiling-point of a liquid with 55 per cent. nitrogen to that of a liquid containing 22 per cent. nitrogen, that is to say, from  $81^{\circ}$  to  $85.3^{\circ}\text{K}$ .

The temperature of the nitrogen leaving the top of the tubes must now be  $81 + 4 = 85^{\circ}\text{K}$ ., which corresponds to a pressure of 2.2 atm. abs., and that of the liquid at *B* should be  $85.3 + 4 = 89.3^{\circ}\text{K}$ ., which requires 2.3 atm.

Thus, with the help of Claude's trays, the same effect can be achieved with 2.3 atm. which formerly required 3.3 atm. Under certain circumstances the power economy thus gained is of paramount importance.

Dephlegmators of various types play an important part in a number

of gas-separating plants. They were first developed in air separation in a process for the production of what is known commercially as 'rich air'. This is a mixture containing from 40 to 60 per cent. oxygen, which is employed to raise the efficiency of combustion in furnaces. To obtain a mixture of this composition, which is of great importance in the manufacture of steel, was one of Linde's original ideas, when he first created low-temperature gas separation; but only in recent years has it become possible to produce rich air at sufficiently low costs to warrant its application in metallurgy.

Dephlegmation is also at the basis of most processes for obtaining pure helium from natural gases (see Chapter XI).

### 3. Rectification

Dephlegmation is a particular and not very efficient application of a much more general principle. A parcel of parallel tubes offers an insufficient surface of interaction between the vapour and the liquid moving inside them. Interaction occurs only along the surface of the tubes and most of the vapour passes up the centre and never enters into interaction with the liquid at all. Moreover, in a dephlegmator the conditions are so ill-adapted to quantitative computation that it is difficult to grasp the essential feature of the process, which is the following: A current of gas and a stream of liquid, which are *not* in equilibrium with one another, are conducted in opposite directions, the surface along which they interact being made as great as possible. Then the vapour will become enriched with the component with the lower boiling-point and the liquid will become richer in the component that boils at a higher temperature. This principle, which is known as *rectification*, is by far the most powerful instrument in the separation of gases.

To grasp the significance of rectification let us turn again to the  $(T, x)$  diagram of oxygen-nitrogen mixtures, as a typical example of a binary solution the boiling-points of whose components lie fairly close together (see Fig. 60). This diagram, which, we must remember, holds for constant pressure, shows clearly that a vapour and a liquid in equilibrium have always different compositions and, conversely, that a vapour and a liquid having the same composition cannot be in equilibrium with one another. Suppose a liquid and a gaseous mixture, both having the same composition and both being in a state of saturation, to be brought into contact. The states of vapour and liquid may be described by the points *A* and *B* in Fig. 60. It is important to

observe that the two phases will be at different temperatures, the vapour being warmer than the liquid. The two phases will mix and eventually reach a state of equilibrium. This state will be characterized by a composition equal to that of *A* and *B* and a temperature between *A* and *B*, and may be depicted by point *C*. The exact position of *C* between *A* and *B* will, of course, be determined by the relative quantities of the mixtures *A* and *B* according to the lever rule. *C* at all events lies in the inhomogeneous region, which means that the resulting vapour and the resulting liquid will lie at the ends of the conodal through *C*, i.e. at *D* and *E*, and will thus have *different* compositions. So if a liquid and a vapour having the same composition are brought into contact, the compositions of liquid and gaseous phase will *move apart*; the liquid will finally contain more and the vapour less of the component with the higher boiling-point. This is the basic phenomenon underlying rectification.

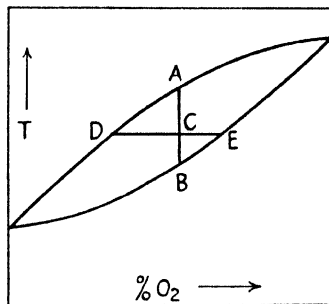


Fig. 60. Illustration of rectifying process on  $(T, x)$  diagram

In order to make the most of this principle, it is essential that the liquid and the vapour be brought into such intimate contact that equilibrium is as nearly as possible attained, as otherwise the ultimate compositions of the two phases will differ less than points *E* and *D* in the figure. It is therefore important to bring about a large surface of interaction between the liquid and the vapour. In practice this is achieved best in the so-called *rectifying column*, in which the vapour is forced through a number of liquid layers.

The simplest type of rectifying column, which is shown schematically in Fig. 61, consists of a vertical copper tube placed above an evaporator. The column is fitted with a large number of plates, which may be of various types. For the present we shall assume that the plates are horizontal disks, perforated with a great number of small holes about 0.8 mm. in diameter. These holes are sufficiently large to enable the vapour to pass through in an upward direction, but the pressure of the vapour from below is sufficiently great to prevent the liquid from escaping downwards through the perforation. The liquid is emitted from one plate to the next through one or more wider apertures fitted with short tubes and furnished with rounded caps that dip into the liquid. The height of the liquid on the plates is determined by the

height of the outlet tubes. In most cases the liquid layer on each plate is about  $\frac{1}{2}$  in. high.

In the simplest type of column the liquid mixture is introduced at *L* from above, after being precooled in the evaporator between *B* and *E* and expanded, trickles down from plate to plate, and is partially evaporated at the bottom of the column. In the stationary state a continuous flow of liquid is maintained in a downward direction, and a continuous current of vapour rises upwards through the liquid. Finally, liquid is emitted at *A* and vapour at *D*.

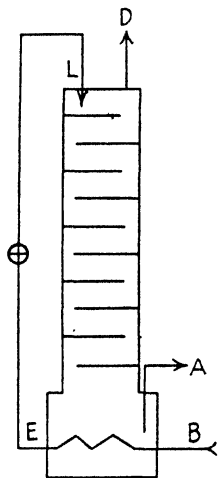


FIG. 61. Simple rectifying column

Since the vapour traverses the plates as a vast number of small bubbles, the size of which is given by the diameter of the perforations, a single plate offers a very large surface of contact between the liquid and the vapour. As a result of this, the two phases may be expected to attain approximate equilibrium on every plate. Thus the liquid trickling off a plate at the bottom and the vapour leaving it at the top will differ in composition by a definite amount. A rectifying plate may be taken as a good example of a separating surface of the kind schematically described in the introduction, and rectification in a plate-column exemplifies

gas separation in a finite number of steps across a corresponding number of surfaces. Of course the surfaces themselves are formed by the interfaces of the bubbles of vapour. The actual metal plate is merely an auxiliary framework which enables the surface to materialize.

The rectifying column sketched in Fig. 61 has a similar drawback to a dephlegmator: it allows only one component of the binary mixture to be obtained in a state of purity. Referring again to the example of atmospheric air, we see that, while a dephlegmator can produce pure nitrogen, but not pure oxygen, a column of this type can give pure oxygen, but not pure nitrogen. For the vapour leaving the column at *D* cannot contain more nitrogen than is in equilibrium with the liquid air entering at *L*. A vapour in equilibrium with atmospheric air at 1 atm. pressure contains 93 per cent. of nitrogen. Purer nitrogen cannot be obtained with this kind of column. To obviate this difficulty the column may be prolonged above the inlet at *L* and fitted with a condenser at the top, as shown in Fig. 62. The condenser maintains a reflux

in the upper part of the column and enables pure nitrogen to be emitted at *D*. However, the condenser requires a source of refrigeration at the top of the column, which is not always easily obtainable. In the figure we have merely hinted at this source by intimating that an amount of heat  $Q$  must be removed from the column at this point. We shall see in Chapter VI how this is achieved in practice.

#### 4. Heat-exchangers and accumulators

Apparatus for distilling mixtures that are liquid at room-temperature are frequently worked intermittently even in large commercial plants. The distiller is charged with liquid and, when empty, recharged at regular intervals. This procedure is never practised in gas separation, mainly owing to the difficulty of storing gases in large quantities in and outside the apparatus. All technical plants for separating gases are worked continuously. For periods amounting to several weeks a steady flow of gas is maintained in the plant, the raw material entering and the products of separation leaving the apparatus at constant velocity, temperature, and composition. The time needed to bring about this stationary state is invariably small compared with that through which the latter is maintained.

Since the gases are separated at temperatures considerably lower than that of the surroundings, the incoming warm gas must be cooled before it enters the actual separating unit, which, as we have seen, may be a condenser, an evaporator, a dephlegmator, or a rectifying column or any combination of these devices. Moreover, the products are mostly required at room-temperature, whereas they emerge from the separating unit as cold vapours or even as liquids. It is therefore natural to utilize the cold outgoing products to precool the incoming warm mixture. This can be effected with inconsiderable losses by means of one of the well-known methods of heat exchange. The exchange of heat between incoming and outgoing gas must not be confused with the refrigeration that is sometimes needed to maintain and always needed to bring about the stationary state of a gas-separating plant operating at a low temperature, and which we shall treat in Chapter V. We are here

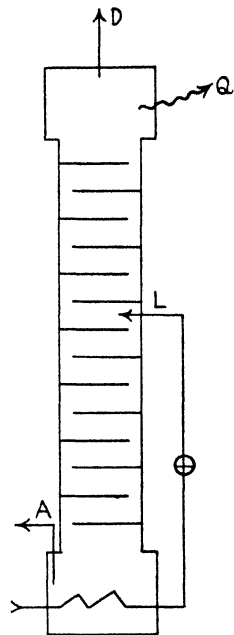


FIG. 62. Rectifying column extended to condenser above inlet



concerned, not with the withdrawal of heat from the plant, but merely with the transfer of heat within the plant.

There are two recognized methods of effecting a transfer of heat within an apparatus, one of which is continuous and the other periodical. The devices employed are respectively the exchanger and the accumulator. In an exchanger two currents of gas, having at the outset different temperatures, are made to flow past each other. Heat is allowed to pass from one to the other until the temperatures are essentially equalized. To prevent the gases from mixing, the two currents are separated by metal walls with a high heat conductivity. The only function of the wall is to keep the gases separate, so that there may be an exchange of heat but no exchange of matter. For precooling warm gases and simultaneously warming up cold vapours the most useful form is the counter-current heat-exchanger, in which the gases move in opposite directions. It consists of a system of tubes so arranged that the two gases have a large surface of contact with the tubes and, through these, with one another. In the case of two gases, a bundle of narrow tubes is usually encased in a single wide tube, and one of the gases traverses the bundle while the other passes around it. The greater the number of tubes in the bundle, the greater will be the surface of contact between the two gases and the more complete will be the exchange of heat, or, which comes to the same thing, the shorter an exchanger need be which is to transfer a certain amount of heat. The bundle usually ends in a perforated plate, to which the tubes are soldered and whence the gas passes to a collector.

These counter-current heat-exchangers are of two distinct types. In one type the necessary surface of contact between the two gas streams is attained by using a very large number of inner tubes; in the second the same result is attained by making the tubes very long. Exchangers of the former type are almost always vertical and essentially the same as the condenser-exchanger shown in Fig. 56. They are usually from 15 to 20 ft. high, and the width of the outer tube depends on the number of inner tubes, which in turn depends on the amount of gas to be transmitted. If the two gas streams are at different pressures, it is customary, for reasons of stability, to pass the gas at the higher pressure through the narrow tubes. But if the pressures are both low, this procedure is frequently reversed. In most cases the incoming gas will have the higher pressure, and if it contains any constituents which may condense or precipitate when the gas is cooled in the exchanger, it is better to pass this incoming gas through the interspace and

not through the narrow tubes. Otherwise the latter may become blocked.

In the second type of exchanger, much fewer inner tubes are used, so that the outer tube is much narrower. It can then be wound to the familiar coil, so that the extensive length required need not take up much space. This helical form of exchanger is used when the incoming gas is at a high pressure. For if a gas at low pressure were passed through very long narrow tubes, the resistance would be so great that a considerable pressure head would develop between the top and the bottom, and this would lead to serious losses and the consumption of additional work.

In a third type of heat-exchanger, first devised by Hampson and later developed by Heylandt, the bundle of narrow tubes is wound spirally within a vertical cylindrical casing, through which the cold gas is allowed to flow. Here the gases no longer flow in counter-current but approximately at right angles to one another. This form of exchanger is very efficient and compact, but rather difficult to calculate.

Let us now consider any type of heat-exchanger and suppose that the warm, ingoing gas is admitted to the bundle of tubes at the top, and the cold, outgoing vapour enters the interspace at the bottom. The exchanger is so dimensioned that the returning gas leaves the top of the interspace at a temperature very slightly below that of the ingoing gas as it enters. The temperature head between the two gases at the bottom of the exchanger must be much greater and is determined by the requirements of the plant.

To understand the functioning of a heat-exchanger, the following facts should be noted:

1. The amount of heat taken up by one gas is equal to the amount of heat withdrawn from the other (plus any heat that may enter from outside through imperfect lagging). In being cooled from  $T'_1$  to  $T'_2$ ,  $m'$  moles of the ingoing gas must give off a quantity of heat

$$Q' = m' \int_{T'_2}^{T'_1} C_p' dT = (H'_1 - H'_2)m',$$

where  $H$  is the total heat or enthalpy of the gas. Similarly, in being warmed from  $T''_2$  to  $T''_1$ ,  $m''$  moles of the outgoing gas must absorb  $Q'' = (H''_1 - H''_2)m''$ . Therefore, neglecting heat losses,

$$(H'_1 - H'_2)m' = (H''_1 - H''_2)m''.$$

Since for a given pressure  $H$  is a function of  $T$  alone, it follows that,

if three of the four temperature points are given, either  $m'/m''$  or the fourth temperature point is determined.

2. In order that the exchanger may work, i.e. that heat may really be transferred from the ingoing to the outgoing gas, the temperature of the former must be greater than that of the latter at every point of the exchanger, and not merely at the ends. If we plot the temperature of the gases as a function of the distance from one end of the exchanger, the two curves can never intersect. For that would mean that, at a certain point of the exchanger, the temperature of both gases would be the same, and then the transfer of heat would cease.

3. The condition  $(H'_1 - H'_2)m' = (H''_1 - H''_2)m''$  is valid not only for the exchanger as a whole but for every section thereof. Suppose the four temperatures at the ends of the exchanger have been fixed and  $m'/m''$  has been determined accordingly. Now consider a section of the exchanger, ending at the top. In this section let the enthalpy of one gas change from  $H'_1$  to  $H'_x$ .  $H'_1$  is fixed and so is  $m'/m''$ .  $H'_x$  can therefore be computed. Only if the resulting  $T'_x < T''_x$  can the exchanger function. We cannot therefore tell whether an exchanger will work merely on the basis of the conditions at its ends. At certain pressures, when the specific heats vary strongly with temperature, this may lead us to serious difficulties.

4. In order that a heat-exchanger may function at all, there must always be a finite temperature head between the gases in a given cross-section. Since, other things being equal, the amount of heat transferred across a given surface is directly proportional to this temperature head, it would seem profitable to make the head as great as possible. On the other hand, we have already stated that this is fraught with the expenditure of additional work. It is therefore not economical to maintain temperature heads in a heat-exchanger greater than are required to have the heat transferred without unduly increasing the surface of contact. In practice, we have to choose an intermediate course: the temperature heads must be kept large enough to ensure the transfer of a sufficient quantity of heat, without making the exchanger too unwieldy, and they must be made sufficiently small so that the losses due to irreversible heat transfer may be kept within reasonable limits.

As a rule, the difference in temperature between the gases at the bottom of the exchanger is determined by the whole process, and it is customary to reduce the temperature head at the top to about 3°C. To secure a sufficient heat transfer, we must bring about as large a surface of contact as possible. This can be done, as we have seen, either

by increasing the length of the exchanger or by increasing the surface per unit length, i.e. the number of tubes. Both these methods tend to make the heat-exchanger heavy and unwieldy.

It is not possible to go into further detail regarding the difficulties of constructing heat-exchangers. The arguments here given were intended merely to bear out the fact, well known to engineers, that the heat-exchanger is not merely one of the most important, but also one of the most complicated and unsatisfactory parts of a gas-separating plant. A light and simple exchanger is inefficient, and an efficient exchanger is cumbersome, complicated, and expensive.

Yet at first sight this method of heat transfer appears greatly superior to what the cold accumulator has to offer. Here the cold is stored in a mass of metal of high heat capacity through which cold gas has passed; whereupon the gas is diverted to another channel and the accumulator traversed by a warm current, which is thus cooled to the low temperature required. A cold accumulator is usually a vertical, lagged tower, filled with a large number of spirally wound strips of corrugated aluminium sheet, packed one above the other. The cold vapour is admitted to the tower from below and, after the current has been shut off, the warm gas enters from above. The tower is thus traversed alternately by two currents of gas in opposite directions. Evidently, to replace a heat-exchanger, we need two accumulators. While the warm gas is traversing one of them, the cold gas passes through the other. The currents are regulated by an automatic valve, which reverses them about every two minutes (Fig. 63).

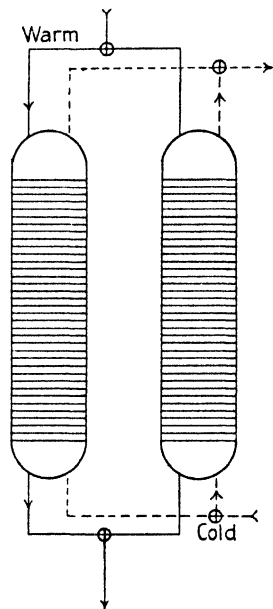


FIG. 63. Pair of cold accumulators with valves for reversing gas current

Cold accumulators were first introduced into the technique of gas separation by Fränkl of the Linde Co. in 1928. The theory was evolved a year later by H. Hausen,<sup>†</sup> also of the Linde Co., and subsequently further developed by S. Gersh in Moscow. It was found that, if a cold and a warm current of gas are alternately passed through an

<sup>†</sup> H. Hausen, *Zeitschr. f. angew. Mathematik und Mechanik*, 9, 173 (1929); *Techn. Mechanik und Thermodynamik*, 1, 219 and 250 (1930).

accumulator, for periods of a few minutes as described above, a stationary state is finally reached after several hours, in which the temperature distribution along the length of the accumulator is practically linear, except in a small portion near the ends (see Fig. 64). Between the end of the warm and the end of the cold period, the straight line giving the temperature as a function of the distance from one end of the

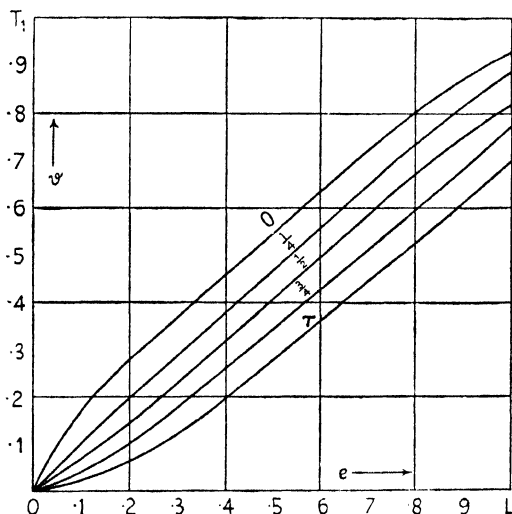


FIG. 64. Temperature distribution  $\vartheta$  for a particular case of a gas passing through an accumulator, after the steady state has been reached, in four phases of the cold period  $\tau$ , as a function of the distance  $l$  from the cold end

$L$  = length of the accumulator;

$T_1$  = temperature of warm gas minus temperature of cold gas at entry.

Cold and warm periods are assumed to be of equal length.

$\vartheta$  is the temperature of the gas, not that of the filling material.

accumulator is merely shifted slightly parallel to itself, as shown in the figure for the case of air being cooled from room-temperature to its boiling-point.

In spite of the complicated nature of this apparatus, the cold accumulator was found to have a number of advantages, as compared with the heat-exchanger. The surface of contact between the gas and the metal, and consequently between the metal and the other gas, for an accumulator of given cross-section, is vastly superior to the corresponding surface in a heat-exchanger. If the accumulator is packed with corrugated aluminium ribbon from 0.2 to 0.6 mm. thick, in spirals 20 mm. high, 1 cub. ft. of packing will produce a surface of heat transfer equal to 2,000 sq. ft.

In this way very small temperature heads can be maintained at the top of the accumulator between the ingoing gas at one period and the outgoing gas in the next, without making the towers too large and heavy. For example, two accumulators for cooling 35,000 cub. ft. of air per hour from room-temperature to  $-180^{\circ}\text{C}$ . were made 10 ft. high and the weight of the aluminium packing was  $1\frac{1}{4}$  tons in each. The temperature heads at the top of the accumulators were less than  $2^{\circ}\text{C}$ .

Owing to the porous character of the aluminium packing, the mechanical resistance of an accumulator is always negligible. Vast quantities of gas can pass, and the resulting pressure head will still be quite insignificant.

Perhaps the most important advantage of the cold accumulator, as compared with the heat-exchanger, is that it enables us to dispense with all appliances for drying the gas before it enters the plant and for removing small quantities of carbon dioxide, which are always present in air and usually occur in other natural and industrial gases. When ordinary heat-exchangers are used, all gases subjected to low-temperature treatment must first be carefully freed from traces of moisture and  $\text{CO}_2$ , as these will otherwise solidify within the plant and block the tubes. This entails the consumption of much caustic potash and occasionally other chemicals, which, in the efficient plant employed in modern gas separation, make up a considerable part of the costs of the process. When cold accumulators are substituted for heat-exchangers, ice and solid  $\text{CO}_2$  are deposited on the aluminium packing and cannot reach the separating unit. In the cold period most of this solid layer is removed by sublimation, so that the accumulators can work for several weeks without becoming clogged, and no chemicals need be consumed in the process.

Nevertheless, cold accumulators have several important disadvantages as compared with heat-exchangers. They are of no use when very pure products are required; for when the current is reversed, the accumulator is full of one gas, which thereupon pollutes the other gas which traverses it in the next period. When a very high degree of purity is needed, heat-exchangers are therefore indispensable. This disadvantage is the more considerable the higher the pressure of the gas. When we consider that accumulators are difficult to construct for high pressures, as the wide towers must then have very thick walls, it is natural that heat-exchangers are preferable when highly compressed gases are treated. The most important field, in which cold accumulators are now widely applied, is that of the production of 'rich air'. It is,

in fact, largely owing to the cold accumulator that this field has been opened up. In this case pure gases are not needed and cheapness is everything. It is a process for which, as we shall see later, high pressures are not required and in which all the particular advantages of the cold accumulator become manifest. It was economy in power, achieved through improved heat exchange, and economy in chemicals, owing to the automatic elimination of moisture and  $\text{CO}_2$  by the accumulators, which enabled air artificially enriched with oxygen to compete with natural atmospheric air in large-scale industry.

## IV

### HEAT, WORK, AND ENTROPY

#### 1. The concept of balance

CONSIDER a gas-separating plant, consisting of one or more of the units described in the last chapter, and suppose a continuous process to be taking place inside it. This process will involve a continuous transfer of matter and heat from one phase to another. It is one of our objects to study this transfer of matter and heat and to determine the laws according to which it occurs. The processes taking place within the plant require the performance of work, generally outside the actual apparatus. This work assumes the form of a compression of the gaseous mixture before it enters the separating units. This expenditure of work is the principal factor in the cost of gas separation and determines, to a great extent, the ultimate price of the pure gases. It is therefore important to conduct the process in such a way as to entail as little work as possible.

It will be shown that the expenditure of a certain amount of work is essential for every separating process, but the work performed in practice is always very much greater than this minimum figure. Part of this 'additional' work is due to frictional losses and imperfect cooling in the compressors and has nothing to do with the construction of the separating units themselves. But a very great portion must be ascribed to processes occurring inside the apparatus. It will be shown that a definite relation exists between every process occurring in some part of the separating plant and the amount of 'additional' work that this process entails, over and above the work that would in any case be necessary to effect a separation of the mixture.

After the apparatus has been cooled down and the separation has begun, a stationary state is reached in which the gaseous mixture enters and the separated products leave at a constant rate, while no further changes occur in the apparatus itself. In the stationary state, not only the apparatus as a whole, but all its parts are completely independent of time. This condition gives rise to a number of important laws, which are usually expressed by so-called *balance equations*. These equations are very useful in studying the processes occurring in separating plants.

*Balance of mass and composition.* Suppose in a given time  $m$  moles of mixture enter the apparatus and  $m_p$ ,  $m_q$ ,  $m_r$ ,... moles leave it as products of separation. In the stationary state there can be no accu-



mulation of matter in the apparatus; the total amount of matter leaving must be equal to the total amount entering. This gives us the equation

$$m = m_p + m_q + m_r + \dots, \quad (1)$$

which is known as the *balance of mass*. Equation (1) is valid, not only for the whole apparatus but for any one of its parts. If  $m_a$  moles of some mixture and  $m_b$  moles of another mixture enter some part of the apparatus in the given time, and if  $m_p$  moles of a third mixture and  $m_q$  moles of a fourth leave this part in the same time, then

$$m_a + m_b = m_p + m_q.$$

What is true of the mixture as a whole is also true of any of its components, none of which can accumulate anywhere when the plant is in a stationary state. If in the mixture of mass  $m$  entering the concentration of one of the components is  $x$ , the total amount of this component entering in the given time will be  $mx$ . If  $m$  is separated into  $m_p$  and  $m_q$ , which may contain concentrations  $x_p$  and  $x_q$  of the component in question, the total amount of this component leaving the apparatus will be  $m_p x_p + m_q x_q$ , and this must be equal to the total amount of the same component entering. This gives us the equation

$$mx = m_p x_p + m_q x_q, \quad (2)$$

which is known as the *balance of composition*. Clearly equation (2) is not limited to two separation products. The masses may be measured in moles or in units of volume or weight, the concentrations correspondingly in mole fractions, volume fractions, or weight fractions, or, of course, in the corresponding percentages.

*Balance of heat.* Consider any part of the apparatus, together with the matter it contains at any moment, and suppose that it is adiabatic, meaning that no heat is given off to or absorbed from other parts of the apparatus or the surrounding medium. Suppose also that the only work done in this part is done against the external pressure. A certain quantity of matter enters in the given time and the same quantity leaves. Let the specific† internal energy of the matter entering be  $u'$ , its specific volume  $v'$ , and its pressure  $p'$ . Similarly, let the specific energy and volume and the pressure of the matter leaving be  $u''$ ,  $v''$ , and  $p''$  respectively. In general several mixtures will enter and leave at different points and the equations will not be limited to two terms. Now if  $\Delta u$  be the increase in specific energy incurred by the substances

† Here and in future a 'specific' quantity will be taken as meaning the value of that quantity for the unit of 'mass', in whatever units the 'mass' is measured. In general, this will be moles. Specific quantities will be denoted by small letters.

in passing this particular part of the apparatus, and  $w$  the amount of work done *on* the substances per unit of mass, then, for an adiabatic process, the first law of thermodynamics gives  $\Delta u - w = 0$ , which leads to the equation

$$u'' - u' + p''v'' - p'v' = 0,$$

or

$$u' + p'v' = u'' + p''v''.$$

Now the expression  $u + pv$  is the specific *total heat* or *enthalpy*  $h$ , so that we may write  $h' = h''$ . Thus, if a number of mixtures of mass  $m_a, m_b, m_c, \dots$  with specific enthalpies  $h_a, h_b, h_c, \dots$  enter a part of the apparatus, and the masses  $m_p, m_q, m_r, \dots$  with specific enthalpies  $h_p, h_q, h_r, \dots$  leave, we may write the equation

$$m_a h_a + m_b h_b + m_c h_c + \dots = m_p h_p + m_q h_q + m_r h_r + \dots, \quad (3)$$

which may be called the *balance of heat*.

If the process occurring in this part of the apparatus is not adiabatic, i.e. if a quantity of heat  $Q$  is introduced from outside, the equation expressing the balance of heat takes the form

$$m_a h_a + m_b h_b + \dots + Q = m_p h_p + m_q h_q + \dots \quad (3')$$

Here for the first time we meet with an equation in which a quantity of heat  $Q$  is added to an enthalpy  $H (= mh)$ , a practice that will be very useful in future calculations. Physically it implies the equivalence of 'heat' and 'enthalpy'. In this conception 'heat' may enter and leave an apparatus in two ways, either by conduction or radiation, as expressed by the term  $Q$ , or in the form of matter flowing in and out and carrying with it a definite amount of enthalpy  $mh$ .

*Balance of entropy.* Suppose that the process occurring in some part of our apparatus is reversible as well as adiabatic. In this case, as we know from the second law of thermodynamics, the entropy of the substances leaving this part of the apparatus will be the same as that of those entering. If  $s_a, s_b, \dots$  be the specific entropies of the substances entering, and  $s_p, s_q, \dots$  the specific entropies of the substances leaving, we obtain the following equation, expressing the *balance of entropy*:

$$m_a s_a + m_b s_b + \dots = m_p s_p + m_q s_q + \dots \quad (4)$$

If the process is reversible but not adiabatic, i.e. if a quantity of heat  $Q$  is introduced from outside by conduction or radiation, this will entail an increase in entropy equal to  $Q/T$ , if  $T$  is the temperature of that part of the apparatus where the heat is introduced. In order that the total entropy in the part considered may remain unchanged, the

substances leaving must carry with them more entropy than those entering by an amount  $Q/T$ . In this case equation (4) assumes the form

$$m_a s_a + m_b s_b + \dots + Q/T = m_p s_p + m_q s_q + \dots \quad (4')$$

If, in addition to the introduction of heat from the outside, the process occurring in this part of the apparatus is irreversible, this will entail a further increase in entropy  $\Delta S_{\text{irr}}$ , so that the entropy carried away by the substances leaving the system will have to be greater still in order to maintain the stationary state. In this general case we may write equation (4) as follows:

$$m_a s_a + m_b s_b + \dots + Q/T + \Delta S_{\text{irr}} = m_p s_p + m_q s_q + \dots \quad (4'')$$

The significance of this irreversible change of entropy will be considered later.

## 2. The $(h, x)$ diagram

Mass, composition, enthalpy, and entropy are the principal quantities which, together with temperature and pressure, determine the processes of gas separation. To obtain a graphical representation of these processes for the case of air, Keesom† made use of the  $(h, s, x)$  surface and its projections on the  $(h, x)$  and  $(h, s)$  planes. Keesom's theoretical work on air has laid down the general line of research as regards the separation of binary mixtures.

Let us consider first the  $(h, x)$  projection. This diagram will contain a dew-curve and a boiling-curve like the  $(T, x)$  and  $(p, x)$  diagrams we have discussed in Chapter II. Every point on the dew-curve will have a corresponding point on the boiling-curve such that a liquid and a vapour whose states are defined by these points are in equilibrium with each other. The lines joining corresponding points, which, as in the case of  $(p, x)$  and  $(T, x)$  diagrams, are known as connodals, will no longer be parallel to the  $x$ -axis, since a liquid and a vapour in equilibrium do not possess the same enthalpy; neither will they be perpendicular to the  $x$ -axis, as the liquid and the vapour will not have the same composition, except in the two limiting cases of  $x = 0$  and  $x = 1$ . The area between the boiling-curve and the dew-curve will again be called the inhomogeneous region.

Since the enthalpy  $h$  of each pure component contains an arbitrary constant, the whole  $(h, x)$  diagram may be freely sheared along the  $h$ -axis, e.g. by maintaining the scale for  $x = 0$  and adding on a constant to the values of  $h$  for  $x = 1$ .

† W. H. Keesom, *Leiden Commun.*, Suppl. 69 a; *Actes du VI<sup>ème</sup> Congrès International du Froid*, Buenos Aires, 1932: *Rapport de la 1<sup>ère</sup> commission*, p. 136.

The  $(h, x)$  diagram, containing dew-curve and boiling-curve, conodals and isothermals, can be constructed for a given pressure if the  $(T, x)$  diagram is known as well as the heats of evaporation of the liquid mixtures and the specific heats of the gas as a function of temperature and composition. As for most mixtures these data are unknown, only

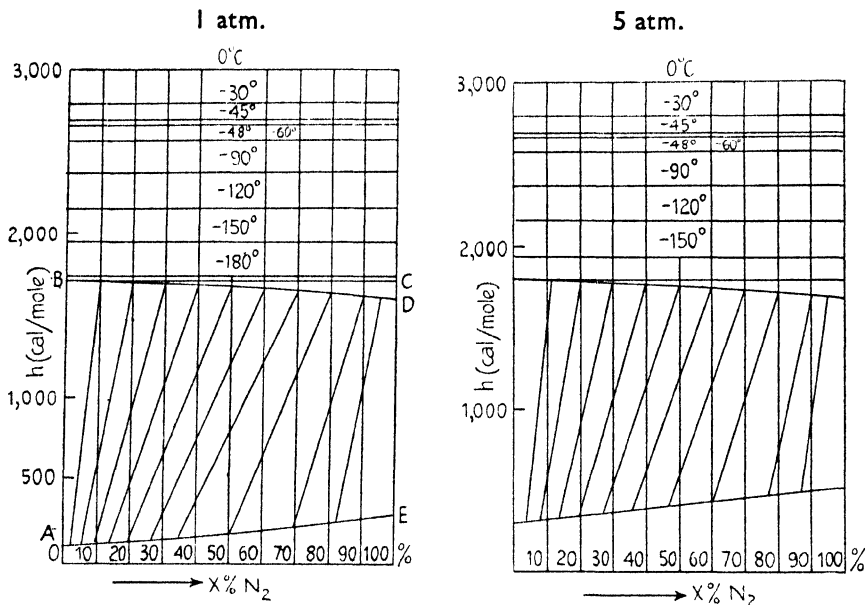


FIG. 65.  $(h, x)$  diagrams of oxygen-nitrogen mixtures at 1 and 5 atm. abs.

two  $(h, x)$  diagrams have as yet been constructed, one by Keesom and Tuyn† for oxygen-nitrogen mixtures, and one by Fedoritenko and Ruhemann‡ for mixtures of nitrogen and helium. The former was worked out for 1 and 5 atm., the latter for 4 and 20 atm. The diagrams are reproduced in Figs. 65 and 66. Tables 10 and 11 (p. 89) give the values of  $h$  in cal./mole for the dew- and boiling-curves of oxygen and nitrogen mixtures. A mole of a mixture containing  $m_1$  moles of a substance with molecular weight  $M_1$  and  $m_2$  moles of one with a molecular weight  $M_2$  is defined as  $(m_1 M_1 + m_2 M_2)/(m_1 + m_2)$  gm. of the mixture. The choice of arbitrary constants for the enthalpies of pure oxygen and pure nitrogen will be given later.

The  $(h, x)$  diagram of oxygen-nitrogen mixtures was determined as follows. First the specific enthalpy of liquid oxygen was chosen as

† W. H. Keesom and W. Tuyn, *Actes*, Buenos Aires: *Rapport de la 1ère commission*, p. 174.

‡ A. Fedoritenko and M. Ruhemann, *Techn. Phys. U.S.S.R.* 4, 1 (1937).

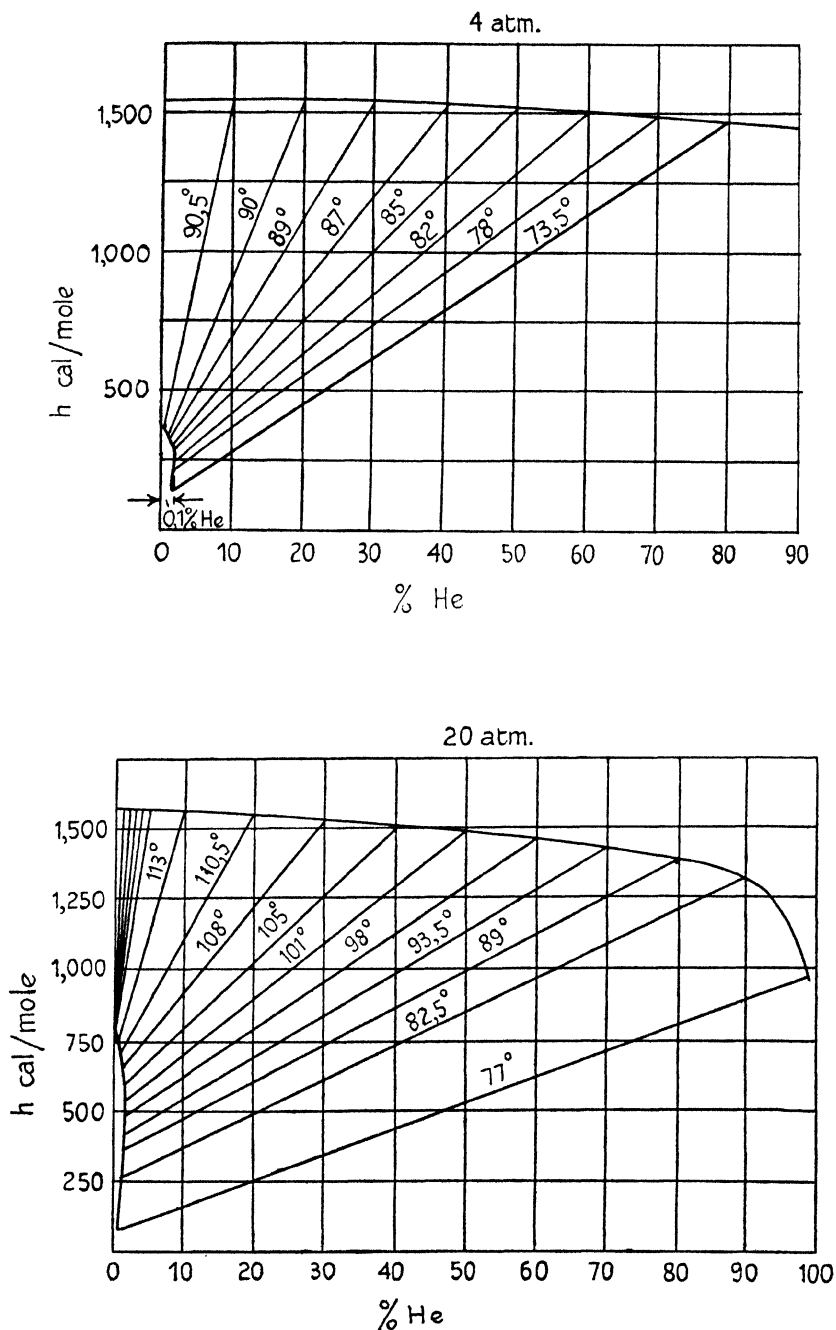


Fig. 66.. ( $h$ ,  $x$ ) diagrams of nitrogen-helium mixtures at 4 and 20 atm. abs.

TABLE 10. *Specific Enthalpy  $h$  in cal./mole for  $O_2$ - $N_2$  Mixtures at 1 atm. along Dew-curve and Boiling-curve*

Mole % $N_2$	Vapour	Liquid
0	1,732	100
10	1,727	110
20	1,722	124
30	1,716	143
40	1,708	163
50	1,700	186
60	1,692	210
70	1,682	235
80	1,670	259
90	1,656	282
95	1,649	294
100	1,641	304

TABLE 11. *Specific Enthalpy  $h$  in cal./mole for  $O_2$ - $N_2$  Mixtures at 5 atm. along Dew-curve and Boiling-curve*

Mole % $N_2$	Vapour	Liquid
0	1,800	314
10	1,793	335
20	1,786	358
30	1,779	380
40	1,771	400
50	1,762	420
60	1,753	442
70	1,743	465
80	1,732	490
90	1,720	514
95	1,713	526
100	1,707	537

100 cal./mole at the boiling-point at 1 atm. pressure. This gives point *A* in Fig. 65. The corresponding point *B* on the dew-curve is obtained by adding the latent heat of evaporation of pure oxygen (1,632 cal./mole) to the ordinate of point *A*. The arbitrary constant in the enthalpy of nitrogen is then fixed by making the enthalpy of pure gaseous nitrogen at the boiling-point of oxygen equal to the enthalpy of pure oxygen vapour at this temperature, i.e. 1,732 cal./mole. This determines a point *C* on the nitrogen axis at the same height as *B*. With the assumption that the enthalpy of a gaseous mixture is a linear function of the enthalpies of the pure components, the isothermal through *B* and *C* becomes a straight line parallel to the *x*-axis. The dew-curve in the (*h*, *x*) diagram is then determined by subtracting from 1,732 cal./mole the value of  $\int_T^{90.1} C_p dT$  at various compositions. The lower limit *T* of the integral is taken from the (*T*, *x*) diagram. The specific heats of the mixture can be obtained from those of the pure components, since the additivity of enthalpies in the gas implies that of specific heats also. The isothermals in the homogeneous region above the dew-curve can be obtained in the same way. The enthalpy of liquid nitrogen at the boiling-point is then determined by subtracting 1,337 cal./mole, the latent heat of evaporation of nitrogen, from point *D* at the end of the vapour-curve. This gives point *E* in Fig. 65. To compute the boiling-curve, the heats of evaporation of the mixture at various concentrations must be known, since there is no justification for assuming additivity of enthalpies in the liquid. We shall treat these heats of

evaporation separately in the next section. For oxygen–nitrogen mixtures at atmospheric pressure, Dana† determined heats of evaporation, giving the vertical distances between points on the dew-curve and boiling-curve. Thus the boiling-curve may be drawn. The connodals can then be inserted from the  $(T, x)$  curves. The diagram for 5 atm. can be determined with the help of the virial coefficients of the pure gases.

To construct the  $(h, x)$  diagram of helium–nitrogen mixtures, Fedoritenko and Ruhemann made use of the  $(T, x)$  curves of this system described in Chapter II, Figs. 50 and 51. In this case the heats of evaporation of the mixtures were not known. However, the solubility of helium in liquid nitrogen is so small that the error incurred by using the value for pure nitrogen is of no consequence.

### 3. Heats of evaporation of binary mixtures

The latent heat of evaporation  $\lambda$  of a pure substance is a well-defined quantity and requires no further specification. Not so the heat of evaporation of a binary mixture. According to the conditions under which the mixture is evaporated, different values may be obtained. Until recently it was impossible to compare latent heats obtained for mixtures by various authors as the conditions of the experiments differed and no theoretical relations were known to exist between the various quantities measured.

In 1933 V. Fischer‡ pointed out that there are five different ways of defining heats of evaporation of binary mixtures and that in the general case all five quantities are different.

Let  $H$  be the total enthalpy of a binary mixture, say oxygen and nitrogen. The specific enthalpy  $h$  is then defined as usual by the relationship

$$h = \frac{H}{n_O + n_N}, \quad (5)$$

where the subscripts O and N refer to oxygen and nitrogen respectively and  $n$  denotes the number of moles present.

Besides the specific enthalpy  $h$  we may now define the *partial molar enthalpies*  $h_O$  and  $h_N$  by the equations

$$h_O = (\partial H / \partial n_O)_{T, p, n_N}; \quad h_N = (\partial H / \partial n_N)_{T, p, n_O}. \quad (6)$$

Now in exactly the same way as, in Chapter II, p. 27, we developed a relationship between the Gibbs potential  $G$  and the chemical poten-

† L. I. Dana, *Proc. Amer. Acad.* **60**, 241 (1925).

‡ V. Fischer, *Ann. d. Physik* (5), **17**, 209 (1933).

tials  $\mu_i$ , we can derive a similar relationship between the total enthalpy  $H$  and the partial molar enthalpies  $h_O$  and  $h_N$ . It has the form

$$H = n_O h_O + n_N h_N. \quad (7)$$

Comparing (7) and (5), we obtain

$$h = x_O h_O + x_N h_N. \quad (8)$$

Now let us suppose that the mixture exists in two phases in equilibrium. Then equation (8) will be valid for each phase separately and,

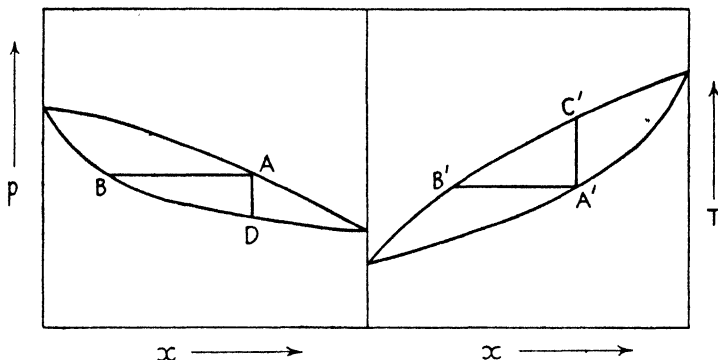


FIG. 67.  $(p, x)$  and  $(T, x)$  diagram to illustrate different latent heats of evaporation

if we denote by the superscripts  $l$  and  $v$  the liquid and the vapour phase respectively, we shall now have the two equations

$$h^l = x_O^l h_O^l + x_N^l h_N^l, \quad h^v = x_O^v h_O^v + x_N^v h_N^v. \quad (9)$$

The latent heats of evaporation of a binary mixture under certain experimental conditions may be expressed as differences between values of  $h^v$  and  $h^l$ , taken at various points in a  $(p, T, x)$  space, and these differences can now be expressed in terms of the concentrations of the two components in both phases, together with the partial molar enthalpies.

Consider the  $(p, x)$  and  $(T, x)$  diagrams of Fig. 67. The difference in enthalpy of a gaseous mixture in  $B$  ( $B'$ ) and a liquid in  $A$  ( $A'$ ) may be defined as the heat of evaporation  $\lambda_{pT}$  at constant pressure and constant temperature. With equations (9) we may thus write

$$\lambda_{pT} = x_O^v h_O^v - x_O^l h_O^l + x_N^v h_N^v - x_N^l h_N^l. \quad (10)$$

The difference in enthalpy between points  $C'$  and  $A'$  in Fig. 67 may be defined as the heat of evaporation  $\lambda_{px}$  at constant pressure and constant composition. If  $h_O^v$  and  $h_N^v$  denote the partial molar enthalpies at  $C'$ , this may be written

$$\begin{aligned} \lambda_{px} &= x_O^l h_O^v - x_O^l h_O^l + x_N^l h_N^v - x_N^l h_N^l \\ &= x_O^l (h_O^v - h_O^l) + x_N^l (h_N^v - h_N^l). \end{aligned} \quad (11)$$



Similarly, the difference in enthalpy between points  $D$  and  $A$  in Fig. 67 is defined as the heat of evaporation  $\lambda_{Tx}$  at constant temperature and constant composition, and

$$\lambda_{Tx} = x_O^l(h_O^{''v} - h_O^l) + x_N^l(h_N^{''v} - h_N^l), \quad (12)$$

where  $h_O^{''v}$  and  $h_N^{''v}$  are the partial enthalpies at  $D$ .

If from many moles of liquid of composition  $x_O^l, x_N^l$  (point  $A$ ) one mole is evaporated, the composition of the resulting vapour,  $x_O^v, x_N^v$  (point  $B$ ), will be in equilibrium with  $x_O^l, x_N^l$ . In this case the required heat of evaporation  $\lambda_{vl}$  may be written

$$\lambda_{vl} = x_O^v(h_O^v - h_O^l) + x_N^v(h_N^v - h_N^l). \quad (13)$$

If from many moles of vapour of the composition  $x_O^v, x_N^v$  (point  $B$ ) one mole of liquid is condensed, the liquid will have a composition  $x_O^l, x_N^l$  (point  $A$ ) in equilibrium with  $x_O^v, x_N^v$ . The negative heat of condensation  $-\lambda_{lv}$  may then be written as follows:

$$-\lambda_{lv} = x_O^l(h_O^v - h_O^l) + x_N^l(h_N^v - h_N^l). \quad (14)$$

It is thus evident that different latent heats may be obtained according to the conditions chosen for the experiment. We are here not concerned with the relationships deduced by Fischer as subsisting between the various values of  $\lambda$ . It could be shown that, at sufficiently low pressures, several nearly coincide. But it is important to note that of the five values defined by Fischer, only four have a physical meaning. For in the formulae (11)–(14) differences of enthalpy appear of the form  $(h_O^v - h_O^l)$  or  $(h_N^v - h_N^l)$  only, the two terms being taken at the same concentrations. However, in formula (10) we have differences of the form  $x_O^v h_O^v - x_O^l h_O^l$ , the two terms having different compositions. But in view of the arbitrary constants contained in the enthalpies of oxygen and nitrogen, the entire  $(h, x)$  diagram may be sheared in respect of the two ordinate axes independently. Then all vertical distances between the two equilibrium curves will remain unchanged, but differences in  $h$  between two points, one on each curve, that are situated at different values of  $x$  will vary with the choice of the constants. Therefore  $\lambda_{pT}$ , since it depends on the values of arbitrary constants, has no physical meaning.

Only in one case have latent heats of binary mixtures been determined accurately. Using a dynamic method, Dana† succeeded in measuring  $\lambda_{px}$  for mixtures of oxygen and nitrogen at atmospheric pressure. With an electric heating coil liquid mixtures of oxygen and nitrogen were

† L. I. Dana, *Proc. Amer. Acad.* 60, 241 (1925).

evaporated from an insulated glass vessel, liquid of constant composition being continuously introduced into this calorimeter. In the stationary state the vapour leaving the apparatus must have the same composition as the liquid introduced. At the same time the liquid in the calorimeter will be enriched with oxygen, so as to be in equilibrium with the escaping vapour. But this liquid does not enter into the process. From the quantity of heat introduced and the amount of vapour leaving the apparatus in a given time,  $\lambda_{px}$  is obtained for the composition of the escaping vapour. Fig. 68 shows a sketch of Dana's apparatus. Fig. 69 gives  $\lambda_{px}$  as a function of the composition.

As has been mentioned, heats of evaporation of other binary mixtures are deplorably lacking and no determinations have as yet been made at higher pressures.

#### 4. Calculations on the $(h, x)$ diagram

The  $(h, x)$  diagram enables us to calculate effects connected with the transport of heat and matter simultaneously. In order to facilitate these calculations, Keesom† introduced a simple analytic method which allows relations involving balance of heat and balance of mass and composition to be expressed in a single equation.

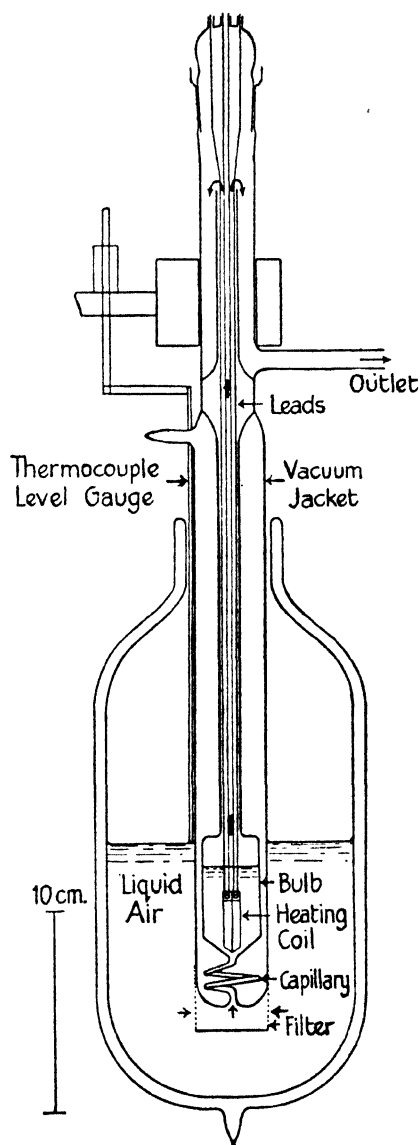


FIG. 68. Apparatus for measuring latent heats  $\lambda_{px}$  of binary mixtures at constant pressure and constant composition

† W. H. Keesom, *Leiden Commun.*, Suppl. 69 a; *Proc. Amsterdam*, **33**, 901 (1930); *Actes du VI<sup>ème</sup> Congrès International du Froid*, 1932: *Rapport de la 1<sup>ère</sup> commission*, p. 136.

At first we shall confine ourselves to processes occurring at constant pressure. A binary mixture in a certain state, which may be denoted by a point  $A$  on the  $(h, x)$  plane, is termed a phase. A phase  $A$  is considered to have three properties, a mass  $m_A$ , a composition  $x_A$ , and a specific enthalpy  $h_A$ . Whereas  $x_A$  and  $h_A$  are represented by the coordinates of the point  $A$  on the  $(h, x)$  plane,  $m_A$  is not represented.

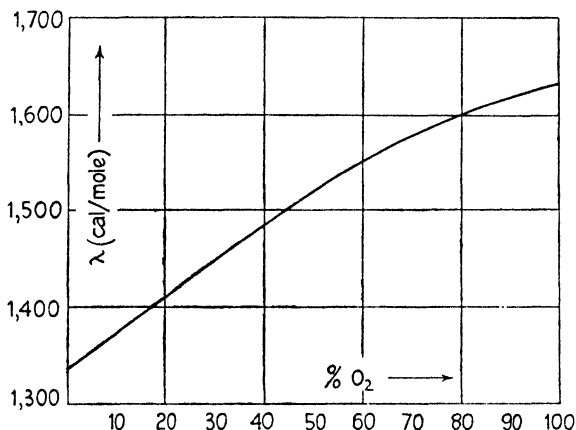


FIG. 69. Latent heat  $\lambda_{px}$  at constant pressure and constant composition of oxygen-nitrogen mixtures at atmospheric pressure

Now suppose two mixtures, having different compositions and enthalpies, which are represented by two points on the  $(h, x)$  plane, to be brought together and mixed. The resulting mixture will obviously have a mass equal to the sum of the masses of the two original mixtures. The resulting composition and enthalpy will be represented by a point on the  $(h, x)$  plane situated on the straight line joining the first two points at the centre of gravity of the masses at these points. This is the same as stating that the positions of the three points will satisfy the lever rule (see Fig. 70).

Moreover, if from  $m_A$  moles of a mixture  $A$  with a composition  $x_A$  and a specific enthalpy  $h_A$  we remove a quantity  $m_B$ , having a composition  $x_B$  and a specific enthalpy  $h_B$ , the remainder, which may contain  $m_C$  moles with the coordinates  $x_C$  and  $h_C$ , will be represented by a point on the projection of the straight line  $AB$  such that  $A$  lies at the centre of gravity of  $B$  and  $C$ . If we bring a mixture  $C$  to a point of the  $(h, x)$  plane situated in the inhomogeneous region for the pressure in question (see Fig. 71), we know that this mixture will separate into a liquid  $A$  and a vapour  $B$ , which will be represented on the diagram

by two points, one on the dew-curve and one on the boiling-curve. They will lie on a straight line (the connodal) through  $C$ , and the relative quantities of liquid and vapour will be such that  $C$  is the centre of gravity of  $A$  and  $B$ . Finally, if a quantity of heat  $Q$  be introduced to a phase  $A$ , mass and composition of the phase will remain unchanged,

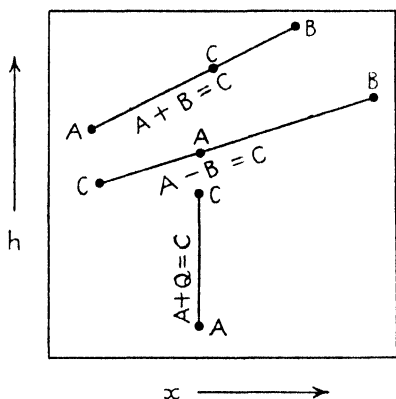


FIG. 70. Addition and subtraction of phases

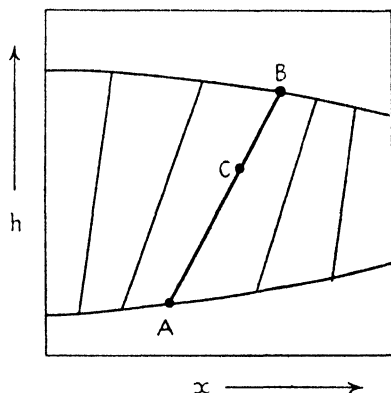


FIG. 71. State in inhomogeneous region as 'sum' of liquid and vapour phase

while its specific enthalpy  $h_A$  will be increased by an amount  $Q/m_A$  (see Fig. 70).

Keesom expresses these obvious physical facts analytically in the following way. A phase  $C$  is defined as the sum or difference of two phases  $A$  and  $B$ , expressed by the equation  $A \pm B = C$ , if the following equations hold:

$$\left. \begin{aligned} m_A \pm m_B &= m_C \\ m_A x_A \pm m_B x_B &= m_C x_C \\ m_A h_A \pm m_B h_B &= m_C h_C \end{aligned} \right\}. \quad (15)$$

A phase  $C$  is said to be the sum or difference of a phase  $A$  and a quantity of heat  $Q$ , expressed by the equation  $A \pm Q = C$ , if the following equations hold:

$$\left. \begin{aligned} m_A &= m_C \\ x_A &= x_C \\ h_A \pm Q/m_A &= h_C \end{aligned} \right\}. \quad (16)$$

These equations express analytically just those geometrical relations which we have described.

To illustrate the practical use of this method we shall take a simple example of a problem of gas separation. Suppose that in a certain time 1 ton of a binary mixture, having a given temperature and pressure, is to be separated into components of specified purity. Suppose that one of these products is to be obtained as a saturated vapour, the other

as a boiling liquid. How the separation is to be effected is of no importance, but we are asked to find how much heat is given off or absorbed in the course of the process.

In Fig. 72 the process is illustrated schematically: a phase  $P$  enters the separator, a gas  $D$  and a liquid  $A$  leave it in the same period of

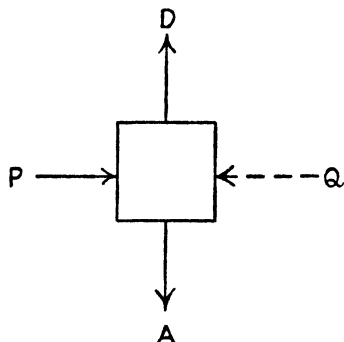


FIG. 72. Schematic separating process

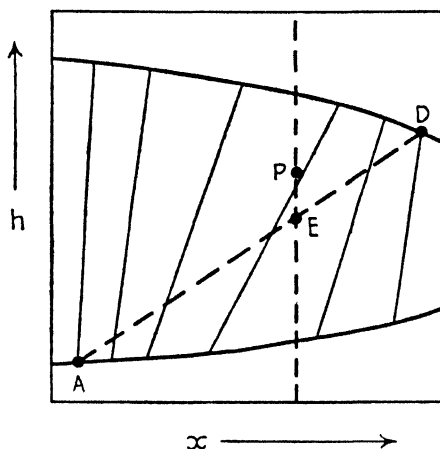


FIG. 73. Process of Fig. 72 on  $(h, x)$  diagram illustrating use of Keesom's method

time. Simultaneously a quantity of heat  $Q$  (positive or negative) is absorbed.

Now consider the process on the  $(h, x)$  diagram (Fig. 73). Suppose  $P$  is a mixture partly gaseous, partly liquid. As its temperature and composition are known we can plot the point on the figure. Similarly, we can plot  $A$  and  $D$  as we know their compositions and that they are situated on the equilibrium curves.

The balance equation for this process is, according to our algebra,

$$A + D = P + Q.$$

Let

$$A + D = E.$$

Then, according to equations (15) and (16),  $E$  is on the straight line  $AD$  with a composition equal to that of  $P$ , and the vertical distance  $PE$  is equal to the value of  $Q$  we are seeking. Since in the figure  $h_P$  is greater than  $h_E$ ,  $Q$  is negative, that is to say, heat must be withdrawn from the system.

In some cases it may be useful to consider on one  $(h, x)$  diagram a process occurring at variable pressure. We may, for instance, plot a series of boundary curves, each valid for a definite pressure; but if we insert all the connodals, the figure will tend to become unreadable.

However, one example of the use of one diagram for two pressures may be interesting. On Fig. 74 the boundary curves and a few connodals are given of some mixture, say at 5 atm. and at 1 atm. Suppose a liquid  $A$  and a vapour  $B$  to be in equilibrium at 5 atm.  $A$  and  $B$  will lie at the ends of a connodal. The phase characterizing the sum of these two mixtures will lie on the connodal at a point  $C$ , and the ratio  $AC:BC$

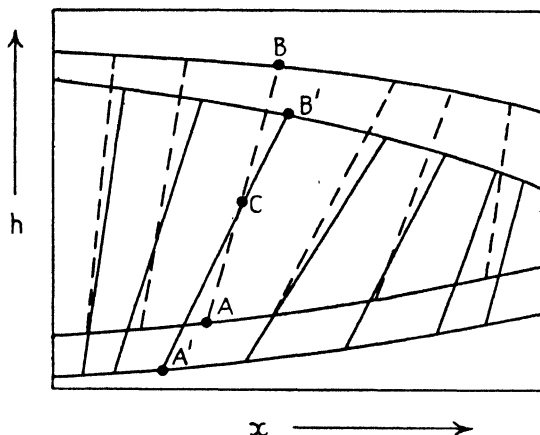


FIG. 74.  $(h, x)$  diagrams for two pressures superposed, showing the result of a change at constant enthalpy on the amount and composition of liquid and vapour phases

will be determined from the quantity of gas and liquid present. Now suppose the two equilibrium mixtures to be expanded in a valve to 1 atm. Under these circumstances the total mass and the total composition of phase  $C$  will, of course, remain unchanged. Moreover, the enthalpy  $h_C$  will also remain unchanged. On an  $(h, x)$  diagram describing states of 1 atm. and 5 atm. simultaneously, point  $C$  will therefore not move as a result of the expansion. However, the liquid and vapour in equilibrium after the expansion will not be represented by the same points  $A$  and  $B$ . These points will shift to  $A'$  and  $B'$  at the ends of the connodal for 1 atm. through  $C$ . Thus the compositions of the two phases, as well as their enthalpies, taken separately, will change. Similarly, as the ratios  $AC:BC$  and  $A'C:B'C$  will in general not be the same, the amount of liquid and the amount of gas present will not be the same after and before the expansion.

A further example, taken directly from a problem of gas separation, brings out still more clearly the uses of Keesom's symbolic algebra. Consider a portion of a rectifying column such that a liquid is introduced from above and a vapour from below (Fig. 75). Inside the

column there will be some kind of interaction between the liquid and the vapour, which we need not specify for the present, and finally a vapour will emerge at the top and a liquid at the bottom. We shall suppose that no heat enters from outside and that the state is stationary.

We can now apply the balance equations developed in the last paragraph and, with our symbolic algebra, we can write down the

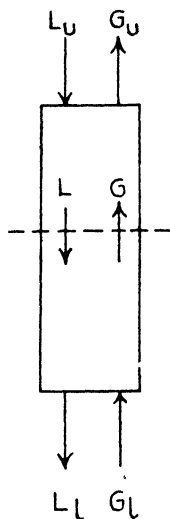


FIG. 75. Portion of rectifying column (schematic) illustrating equivalent current

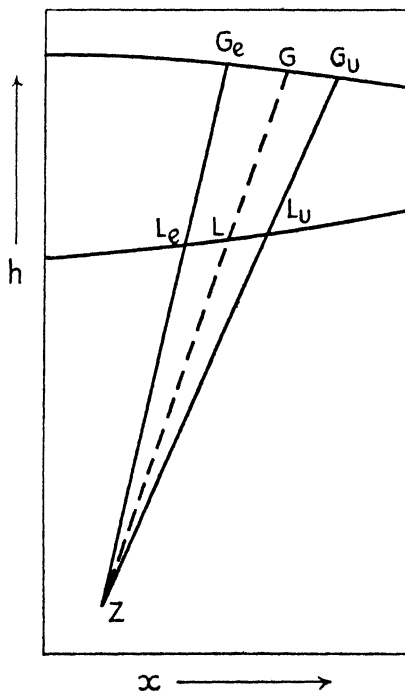


FIG. 76.  $(h, x)$  diagram illustrating equivalent current

balance of mass, composition, and heat in a single equation as in the last example.

Let the suffix  $u$  refer to the top of the apparatus and the suffix  $l$  to the bottom. Then the liquid entering above will be  $L_u$  and that leaving below will be  $L_l$ . Similarly,  $G_u$  is the vapour leaving at the top and  $G_l$  the vapour entering at the bottom. Then

$$L_u + G_l = L_l + G_u,$$

or

$$L_u - G_u = L_l - G_l = Z.$$

On the  $(h, x)$  diagram  $Z$  is the point of intersection of the straight lines through  $L_u, G_u$  and  $L_l, G_l$ , as shown in Fig. 76. Now, if we consider any

horizontal section of the apparatus and determine the amount, composition, and enthalpy of the liquid and vapour entering and leaving this section in a given time, we shall obtain exactly the same equations. The difference between the liquid and gaseous 'phases' entering the section will be equal to the difference between the liquid and gaseous phases leaving the section and will in turn be equal to  $Z$ . The phase  $Z$  is usually known as the equivalent down-current, and we may sum up our results by saying that the equivalent down-current remains unchanged throughout any adiabatic piece of apparatus in so far as no substances are admitted or withdrawn on the way. The phase

$$G - L = R = -Z$$

is called the effective up-current and is, of course, similarly a constant. It is customary to choose equivalent phases the masses of which are positive. Accordingly, if more liquid flows down than vapour flows up, we shall speak of an equivalent down-current and vice versa. As these equivalent currents are mathematical definitions and as such not bound to have physical significance, we need not be surprised if we occasionally come upon such currents with concentrations less than 0 or greater than 1 or with negative enthalpies. We may be sure that all phases actually emerging from the apparatus or present as homogeneous entities will always have 'rational' components.

### 5. The $(h, s)$ diagram

Keesom and Tuyn† constructed the  $(h, s)$  and  $(s, x)$  projections of the  $(h, s, x)$  surface for oxygen-nitrogen mixtures. For the details of the construction we must refer the reader to the original paper. In Fig. 77, which shows the three projections for 1 atm. pressure, the entropy of boiling liquid oxygen is taken as zero. Then the entropy of saturated pure gaseous oxygen is  $\lambda_0/T$ , where  $\lambda_0 = 1,632$  cal./mole is the heat of evaporation of oxygen, and  $T = 90.1^\circ\text{K.}$ , the boiling-point of oxygen. This gives for the entropy of saturated gaseous oxygen  $s_1 = 18.11$  cal./deg. mole. The entropy of pure gaseous nitrogen at  $90.1^\circ\text{K.}$ , i.e. at the boiling-point of oxygen, is taken as  $s_2 = 38.11$  cal./deg. mole, which makes  $s_2 - s_1 = 20.0$  cal./deg. mole.

Before we can begin to use the  $(h, s)$  diagram we must remember that the sum and difference of two phases have not been defined for this projection. In equations (15) and (16) of the last section no mention was made of entropy. Now these two sets of equations could be amplified with the help of the balance equations (4)-(4") in § 1 of this chapter.

† W. H. Keesom and W. Tuyn, loc. cit.



We could, if we liked, consider a phase as consisting not of three but of four component parts  $m$ ,  $x$ ,  $h$ , and  $s$ , and could define the sum and difference of two phases with the help of equations (4)-(4") so as to include entropy. But if we did this the equations (15) and (16) of the

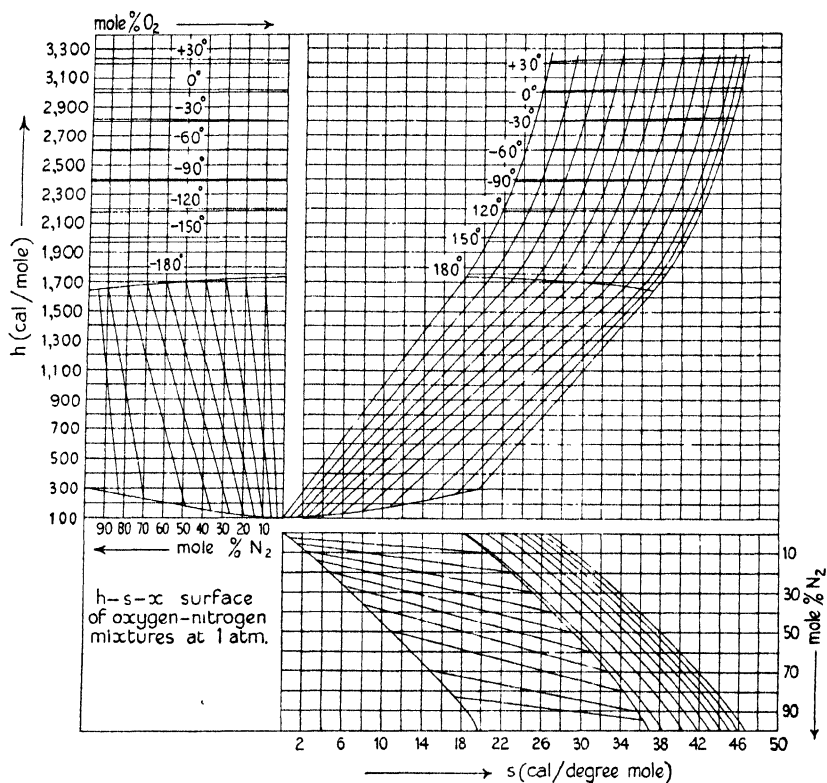


FIG. 77.  $(h, x)$ ,  $(h, s)$ , and  $(x, s)$  projections of the  $(h, s, x)$  surface for mixtures of oxygen and nitrogen at 1 atm.

last section would be valid only for isentropic processes. For all other processes, instead of

$$A + B = C,$$

we should have to write

$$A + B + \Delta S = C,$$

in which  $\Delta S$  is the increase of entropy occurring in the course of the process. Similarly, the equation

$$A + Q = C$$

would now read

$$A + Q + T \Delta S = C.$$

This would greatly complicate our calculation, which would thus lose its principal virtue of simplicity.

To understand this clearly we must realize that we have in fact employed the equation  $A + B = C$  in two distinct senses:

- (1) the two phases  $A$  and  $B$  may be considered equivalent to a single phase  $C$ , which is mathematically defined as their sum;
- (2) the two phases  $A$  and  $B$  will, if brought together, form a single phase  $C$ , or, conversely, the phase  $C$  will separate into two phases  $A$  and  $B$ .

(1) is merely a useful mathematical operation, whereas (2) refers to a definite physical occurrence. The whole force of the equation  $A \pm B = C$  is that it may have either of these two meanings, that we need not, in applying it, worry whether the two phases really do combine to form a single phase or whether we are simply combining them on paper to simplify our calculations. It is, in fact, quite immaterial for this equation whether the two phases are interacting or, on the contrary, completely isolated from each other. It would be unwise to forgo this advantage by introducing new equations.

Now it is clear that, as long as our two phases are combined simply 'on paper', but in point of fact are not interacting at all, the entropy of their sum will be equal to the sum of their entropies. For this case we can complete equation (15) as follows:

$$\begin{array}{l}
 A \pm B = C \\
 \text{if} \quad \left. \begin{array}{l}
 m_A \pm m_B = m_C \\
 m_A x_A \pm m_B x_B = m_C x_C \\
 m_A h_A \pm m_B h_B = m_C h_C \\
 m_A s_A \pm m_B s_B = m_C s_C
 \end{array} \right\} \quad (15')
 \end{array}$$

In this case a point giving the sum or difference of two phases will lie on the straight line joining the two phase-points (or on its projection) in the  $(h, s)$  diagram also. But when the two phases  $A$  and  $B$  interact, the entropy of the sum will in general differ from the sum of the entropies. The sum and difference of two phases would then not lie on the straight line joining the phase-points, and in this case the equation will not be applied at all. The rules of addition and subtraction will be considered to include entropies *only* when the addition and subtraction is a mathematical combination of two phases that do not interact, but *never* when the sum or difference are considered as the results of interaction.



to entropy. *The distance parallel to the s-axis between the points  $L_u-G_u$  and  $L_l-G_l$  will, in fact, give us the change in entropy undergone by the equivalent current in passing through the apparatus.* Since in our example the process is regarded as adiabatic, this change of entropy must be irreversible. By carrying out this construction at various points of our separating plant we can thus determine the irreversible entropy increase taking place at each point of the apparatus.

## 6. Net work and irreversible entropy

We shall now derive the relation between the changes of entropy undergone by mixtures in the interior of a separating plant and the work necessary to carry out the separation process. More especially we shall show what part of the total work is inherent in the actual act of separation and what part is due to irreversible changes which could in principle be eliminated by a suitable reconstruction of the plant.

Hausen† has shown how a completely reversible separating plant can at least be conceived. All practical pieces of apparatus are more or less successful approximations to this ideal separator. We shall see that, the closer we approximate to a reversible process, the smaller will be the work or, as it is frequently termed, the power input required.

Consider an apparatus for separating a gaseous mixture, placed in an environment which is at a constant temperature  $T_0$ . The mixture may have any number of components, but for simplicity we shall assume that there are only two. Heat may be introduced or withdrawn at any number of points. We shall here assume that a quantity of heat  $Q$  (positive or negative) is introduced into the system in a reversible manner. Let us suppose that a stationary state has been reached. We assume that in a given time a volume of gas  $V_1$  is introduced at a pressure  $p_1$  and a volume  $V_2$ , consisting of products of separation, is withdrawn at  $p_2$ . It will in general be useful to include in what is termed the 'apparatus' any compressors that take part in the process. Frequently  $p_1$  and  $p_2$  will both be atmospheric pressure, but this is by no means essential.

If  $W'$  is the work done *on* the system, which incurs an increase in internal energy  $\Delta U$ , then

$$W' = \Delta U - Q. \quad (18)$$

Now  $W'$  may be of two kinds, work done by the compressors and work done by the atmosphere. We are here interested only in the first item, which is often called the *net work*, since it is only this net work that

† H. Hausen, *Zeits. f. techn. Physik*, **13**, 271 (1932).

requires an input of power. We shall denote the net work by  $W$ .† Since the work done by the atmosphere is  $-\Delta pV$ ,

$$W = W' + \Delta pV = \Delta U + \Delta pV - Q = \Delta H - Q, \quad (19)$$

where  $\Delta H$  is the difference in enthalpy between the separated gases and the original mixture.

Now let  $S$  be the entropy of the apparatus and all that is in it, and let  $S_0$  be the entropy of the surroundings, which we have assumed to be at a temperature  $T_0$ . Then

$$\Delta S + \Delta S_0 \geq 0. \quad (20)$$

Since heat exchange with the surroundings is reversible,  $\Delta S_0 = -Q/T_0$ . Therefore

$$\Delta S \geq Q/T_0. \quad (21)$$

If the entire process occurs reversibly,  $\Delta S = Q/T_0$ , and equation (19) yields

$$W_{\text{rev}} = \Delta H - T_0 \Delta S. \quad (22)$$

This is known as the *reversible work of separation*.

In practice irreversible changes occur in a separating plant. In this case  $\Delta S > Q/T_0$  and we may write

$$\Delta S = Q/T_0 + \Delta S_{\text{irr}}. \quad (23)$$

Then

$$Q = T_0 \Delta S - T_0 \Delta S_{\text{irr}},$$

and

$$W = \Delta H - T_0 \Delta S + T_0 \Delta S_{\text{irr}}, \quad (24)$$

or

$$W = W_{\text{rev}} + T_0 \Delta S_{\text{irr}}. \quad (25)$$

We see that every irreversible change of entropy occurring in the apparatus requires the expenditure of an additional amount of work  $W_{\text{irr}} = T_0 \Delta S_{\text{irr}}$ .

Equations (22), (23), and (24) show us the simple relations that exist between enthalpy, entropy, and the work of separation. By determining the change in enthalpy and entropy, undergone in various parts of the plant, we can calculate the work needed to separate the mixture. Moreover, since the formulae allow us to distinguish between reversible and irreversible entropy changes, we can find out which parts of the apparatus are responsible for the greatest entropy increments and accordingly for an increased power input, as compared with that necessary in an ideal, reversible separating plant.

† In most text-books the net work is called  $W'$  and the total work  $W$ . It seemed preferable to reverse the terms here as it is the net work that features in all the calculations and is the more important quantity from the point of view of the engineer.

## REFRIGERATION

**1. Refrigeration, liquefaction, and separation**

THE withdrawal of heat from a substance which is itself at a lower temperature than its surroundings is known as refrigeration. Every process which takes place below room-temperature requires some form of refrigeration, firstly to produce and secondly to maintain the low temperature.

In the usual form of refrigerator a working substance called the refrigerant is made to absorb heat from another substance, which may be apples or butter, and which is thus maintained at a temperature below that of the surroundings. A certain amount of heat is given off by the refrigerant to the surroundings and a certain amount of work is done on the refrigerant.

The refrigerant is generally a system which is wholly or partly in the gaseous state at room-temperature and atmospheric pressure, and partly or wholly liquid at some point in the refrigerating process. This is because a gas, in view of its great compressibility, can have much work performed upon it without requiring high pressures, and because the transition from a liquid to a vapour and vice versa, in view of the latent heats involved, is coupled with the absorption and delivery of large quantities of heat. The refrigerant itself, after the work has been performed upon it and after it has absorbed heat from the substance to be cooled and delivered heat to the environment, is back in the state in which it was at the outset. It has passed through a refrigerating cycle and is now ready to pass through the same cycle again.

When the refrigerating process consists in liquefying a gas it is frequently unnecessary to employ a separate refrigerant. The gas that is to be liquefied can itself serve as the refrigerant or working substance. Thus, in the usual type of liquid-air plant, of which we shall have more to say later, the air itself is the working substance. While part of the air that enters the plant is liquefied, the other part leaves at room-temperature, after having served as a refrigerant to liquefy the first part. When a quantity of air enters a liquefier we cannot state which individual molecules are going to serve as refrigerant and which are destined to be converted into liquid air, although we can compute how much of the ingoing air will actually be liquefied. This state of things makes it rather difficult to understand the workings of a gas liquefier.

Since it is not always easy to distinguish between what is cooling and what is being cooled, it is customary to treat these plants as if they were not refrigerators at all, thus completely veiling the real nature of the process. We shall attempt to avoid this mistake and bring out, as far as possible, the characteristic points of refrigeration in the liquefaction and separation of gases.

Suppose that we desire to cool a substance from a temperature  $T_1$ , say room-temperature, to a temperature  $T_2 < T_1$ . To do this we shall have to give off a certain amount of heat  $-Q_1$  to the surroundings and a certain amount of work  $W'$  will have to be performed. Then

$$W' = \Delta U - Q_1,$$

where  $\Delta U$  is the increase in internal energy of the substance. Actually  $\Delta U$  is negative. As in the case treated at the end of the last chapter, part of this work may be done by the atmosphere, and to this we do not have to contribute. The net work will therefore again be

$$W = \Delta U + \Delta pv - Q_1 = \Delta H - Q_1.$$

On the other hand,  $\Delta S \geq Q_1/T_1$ .

So we have again, as in the last chapter,

$$W \geq \Delta H - T_1 \Delta S.$$

If the process consists in cooling and finally liquefying a gas, the expression

$$W_{\text{rev}} = \Delta H - T_1 \Delta S$$

is called the *reversible work of liquefaction*. It is the minimum work needed to convert the gas into a liquid, starting at room-temperature, and is quite independent of whether a special refrigerant is used or not, depending merely on the enthalpy and entropy of the substance to be cooled. The change of enthalpy  $\Delta H$  to be brought about is called the required *refrigerating performance*.

At first sight it would appear that a plant for separating a gaseous mixture, in which, as a rule, the mixture enters and the products leave at room-temperature, is not a refrigerator at all. The term  $\Delta H$  in equation (24) of p. 104 is negligibly small as compared with the other terms; in the case of perfect gases it is indeed zero. Apparently gas separation as such requires no refrigerating performance. However, the presentation given in Chapter IV was not quite accurate. We there assumed that the heat introduced and withdrawn from the system was transferred reversibly. This is not the case in practice. Actually there will always be an irreversible heat transfer from the warm environment to those parts of the plant that are at low temperatures. These heat

leaks can never be eliminated completely and require permanent compensation. It is the compensation of these losses, i.e. the maintenance of the low temperatures in the plant, that requires a constant refrigerating performance in the stationary state, in the same way as this is required of an ordinary refrigerator in the kitchen. This may be expressed very simply by means of a balance equation. Suppose 1 lb. of refrigerant, which may or may not be the gas that is being liquefied, to be circulating through the apparatus in a given time. Let  $h_1$  be its specific enthalpy on entering the plant and  $h_2$  its enthalpy on leaving. And suppose that an amount of heat  $q$  leaks into the plant during the same time. Then, in the stationary state, the balance of heat requires that  $h_2 - h_1 = q$ . The enthalpy of the gas leaving must be greater than that of the gas entering the apparatus and the required refrigerating performance per pound of refrigerant is  $q$ .

In practice the gas will leave the plant slightly below room-temperature, owing to imperfect heat exchange. This will also require compensation in the form of additional refrigerating performance.

During the period of cooling, before the stationary state is reached, a gas-separating plant is clearly a refrigerator in the ordinary sense of the word. Usually the refrigerating performance in this period is much greater than in the stationary state.

Finally, it may be expedient to withdraw some of the products of separation in the liquid state, as in the liquid oxygen industry. In this case a very much greater refrigerating performance is required, equal to the difference in enthalpy of gaseous oxygen at room-temperature and atmospheric pressure and liquid oxygen at its boiling-point.

We see that every gas-separating plant requires a certain amount of refrigeration, though the amount will differ appreciably according to the type of plant we have in mind.

In recognizing that refrigeration necessitates the expenditure of work and the delivery of heat to the environment, we have as yet accomplished little. For, of course, not every expenditure of work and delivery of heat will lead to refrigeration. We have still to show how these operations may be so coordinated as to result in the lowering of the temperature of a body and in the withdrawal of heat therefrom.

Two types of apparatus are employed in refrigerating engineering, known respectively as compression and absorption engines. Only the former type will concern us here, as the absorption method has so far not been used at the very low temperatures needed for gas separation. In the refrigerating processes that we shall treat, the refrigerant is a gas



at room-temperature and atmospheric pressure and may or may not be identical with the mixture that is being separated or with one of the products of separation. For the following arguments this is of no importance, and we shall treat the gas as a refrigerant irrespective of its subsequent destination or past history.

## 2. Thermodynamic diagrams

We have seen that separation and refrigeration require a definite expenditure of work, which is a function of the enthalpy and entropy of the substance to be treated. It has been shown that separation can be suitably represented on a diagram involving enthalpy, entropy, and composition. Refrigerating processes are usually not connected with changes of composition: either the refrigerant is itself a pure substance or, as in the case of air, its composition remains practically unchanged while it is being cooled or liquefied. The diagrams employed in studying refrigerating processes will therefore be able to dispense with concentration as a variable.

The most important variables of refrigerants are pressure, temperature, enthalpy, and entropy. For certain purposes volume is also useful. These properties can be arranged in several diagrams, two variables being taken as ordinates and abscissae, and the lines on the diagrams representing constant values of the other variables. The most frequent diagrams are  $(h, T)$ ,  $(\log p, h)$ ,  $(T, s)$ , and  $(h, s)$ . Though all complete diagrams are theoretically equivalent, some are more convenient for some purposes and some for others.

The values of  $h$ ,  $s$ , and  $v$  as functions of  $p$  and  $T$  can be obtained by simple differentiation from the characteristic potential of these two variables, which is the Gibbs potential  $g = u - Ts + pv$ . For

$$s = -\left(\frac{\partial g}{\partial T}\right)_p, \quad h = T - T\left(\frac{\partial g}{\partial T}\right)_p, \quad \text{and} \quad v = \left(\frac{\partial g}{\partial p}\right)_T. \quad (1)$$

So, whether or not the Gibbs potential is actually evaluated, the data needed to construct a thermodynamic diagram are the same as those needed to calculate  $g$ . Now, apart from arbitrary constants,

$$g(p, T) = \int_{p_0}^p v(p, T) dp - T \int_{T_0}^T \frac{dT}{T^2} \int_{T_0}^T c_p(p_0, T) dT, \quad (2)$$

where  $p_0$  and  $T_0$  are any chosen pressure and temperature and  $c_p$  is the specific heat at constant pressure. The data needed are therefore (1)  $v(p, T)$ , i.e. an 'equation of state' valid in the whole interval of

pressure and temperature with which we are concerned, or  $(p, v, T)$  relations equivalent to such an equation of state; (2)  $c_p$  as a function of temperature for one arbitrarily chosen pressure.

Now there is no objection to choosing  $p_0$  so low that the vapour may be considered as a perfect gas. Then the calorimetric measurement of  $c_p$  can be replaced by a theoretical value, taken from statistical mechanics. The evaluation of  $g$ , and therefore of  $h$  and  $s$ , is thus possible on the basis of accurate  $(p, v, T)$  measurements alone. Nor is it necessary to calculate  $g$  first in order to obtain  $h$  and  $s$ . Thus, for a diatomic gas we can assume that  $c_p = \frac{7}{2}R$ , irrespective of temperature at  $p = 0$ .† With the relation

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad (3)$$

we can then calculate  $c_p$  for all pressures and temperatures. This enables us to compute  $h$  by integrating  $c_p$  at constant pressure over the temperature interval required. We can find  $s$  from  $c_p$  and our  $(p, v, T)$  relations by using

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T} \quad \text{and} \quad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p, \quad (4)$$

if  $v$  as a function of  $p$  and  $T$  is assumed to be known.

Generally  $(p, v, T)$  data are not known with sufficient accuracy over the whole interval of pressure and temperature, and  $h$  as a function of  $p$  and  $T$  can be determined from the following data:

- (1) a single  $(p, v)$  isothermal, usually at room-temperature;
- (2) the vapour pressure or saturation curve;
- (3) the latent heat of evaporation  $\lambda$  as a function of temperature;
- (4) one of the following three partial derivatives, determined over a wide field of temperature and pressure:
  - (a) the specific heat at constant pressure  $c_p = (\partial h / \partial T)_p$ ;
  - (b) the Joule-Thomson coefficient  $\mu = (\partial T / \partial p)_h$ ;
  - (c) the isothermal expansion coefficient  $\alpha = (\partial h / \partial p)_T$ .

Specific heats of gases are not easy to determine accurately and method (a) has not so far been employed. Though the determination of  $\mu$  is difficult and involves rather complicated apparatus, the method has been very carefully developed and yields accurate results. The

† With the exception of hydrogen, the rotational degrees of freedom of diatomic gases are fully excited at the temperatures concerning us. Vibrational degrees of freedom need not be taken into account.

work of Hausen† and of Roebuck and Osterberg‡ has furnished valuable and extensive data on the Joule-Thomson coefficient, so that method (b) is considered the most reliable for evolving thermodynamic diagrams. A method for measuring  $\alpha$  was developed some years ago by Eucken, Clusius, and Berger.|| It was used by them to compile an ( $h$ ,  $T$ ) diagram of methane.

Hausen evolved an ( $h$ ,  $T$ ) diagram of air from his own measurements of  $\mu$  as follows. Choosing the arbitrary constant in  $h$  so that  $h = 50$  cal./gm. at  $p = 0$  and  $T = 0^\circ \text{K.}$ , and assuming  $c_p = 7R/2M = 0.241$  cal./deg. gm. at  $p = 0$ , where  $M$  is the molecular weight of air, he obtains for the line of constant pressure zero on the ( $h$ ,  $T$ ) diagram (see Fig. 79)

$$h = 50 + 0.241T \text{ cal./gm.}$$

The other lines of constant pressure in the gaseous region are then obtained from the experimental values of  $\mu$  with the relation

$$T_2 - T_1 = \Delta T = \int_1^2 \mu \, dp. \quad (5)$$

The vapour branch of the boundary line from  $A$  to point  $B$  having a horizontal tangent is obtained in the same way, taking the integral of  $\mu$  from the saturation temperature to  $p = 0$ . The liquid branch from  $A'$  to  $B'$  is then plotted from the known heats of evaporation. Curves of constant pressure to the right of  $A'B'$  are constructed by integrating  $\mu$  from the high-pressure side to the boundary curve. To obtain the part of the boundary curve to the right of  $BB'$  we must combine latent heats with integrated values of  $\mu$ . For a given pressure we know the corresponding temperature on the saturation curve as well as the corresponding value of  $\lambda$ . This gives us two points  $C$  and  $C'$ , whose distance from each other we know, as well as their distance from the ordinate axis; but we do not yet know their height above the axis of abscissae. We can obtain the length of two lines  $DC$  and  $D'C'$  by integrating  $\mu$  from a certain high pressure to the saturation pressure at  $CC'$ . We now have a group of four points  $DCC'D'$ , which we know but for the height of the group as a whole above the axis of abscissae. We can then determine other such groups, which must finally be so arranged that the boundary line, as well as the line of constant pressure on which the  $D$ 's lie, become smooth curves. This can be done with

† H. Hausen, *Forsch. auf dem Geb. des Ingenieurwesens*, 1924, 274.

‡ J. R. Roebuck and H. Osterberg, *Phys. Rev.* **48**, 450 (1935).

|| A. Eucken, K. Clusius, and W. Berger, *Zeits. f. Kälteindustrie*, **41**, 145 (1935); *Zeits. f. techn. Physik*, **6**, 267 (1932).

sufficient accuracy and the  $(h, T)$  diagram with lines of constant pressure can thus be completed.

The entropy may then be obtained as follows:

$$\text{Since} \quad ds = c_p dT/T - (\partial v/\partial T)_p dp, \quad (6)$$

we have for a given temperature

$$s = s_0 - \int (\partial v/\partial T)_p dp, \quad (7)$$

where  $s_0$  is an arbitrary constant, which is so chosen that, for  $p = 1$  atm.,

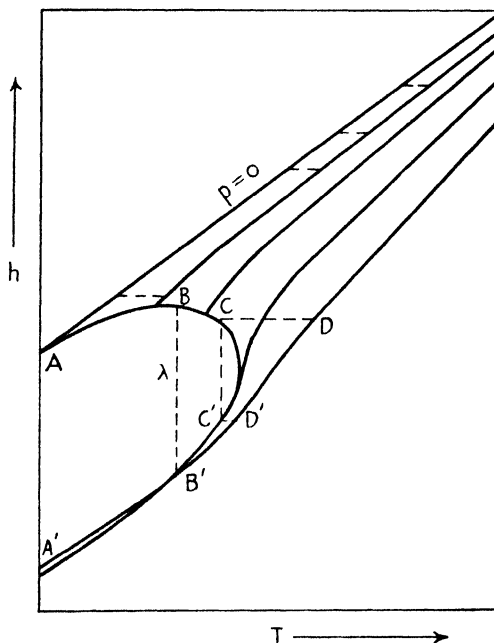


FIG. 79. Construction of  $(h, T)$  diagram

the entropy of liquid air at the boiling-point is zero. For room-temperature the isothermal for air is very accurately known, and so  $\int (\partial v/\partial T)_p dp$  can be computed accurately for this temperature. Now at constant pressure

$$ds = c_p dT/T = dh/T. \quad (8)$$

So, as we know  $s$  for all values of  $p$  at room-temperature, we can compute it for all other temperatures and pressures from the  $(h, T)$  diagram by taking

$$s = s_c + \int_{T_c}^T dh/T. \quad (9)$$

We can now insert the lines of constant entropy in the  $(h, T)$  diagram and also construct a  $(T, s)$  diagram with lines of constant enthalpy.

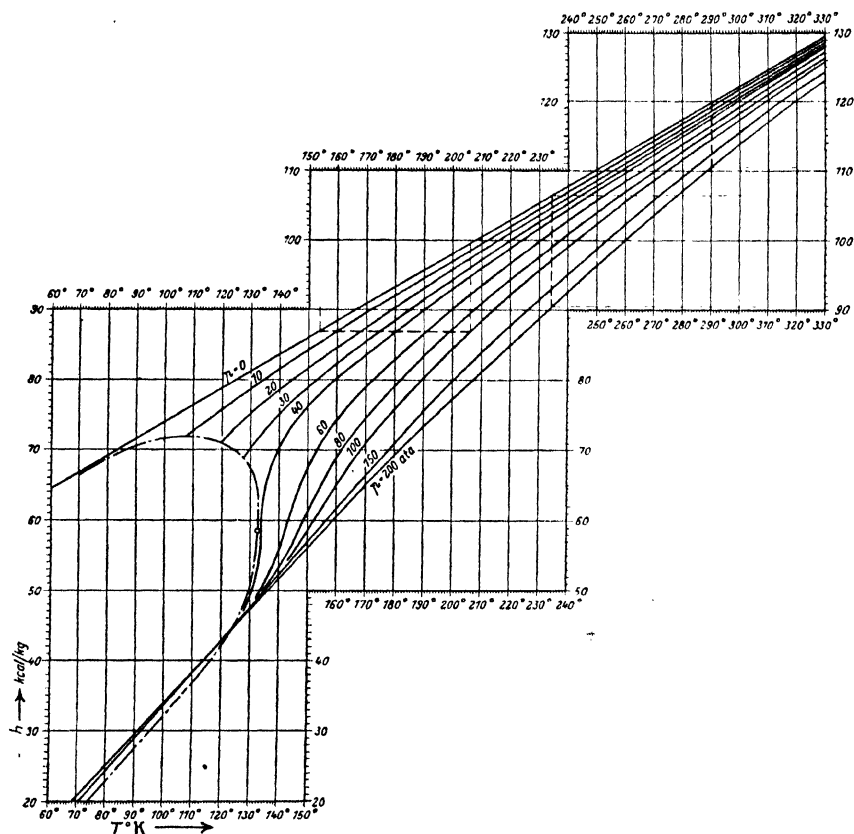


FIG. 80.  $(h, T)$  diagram of air. After H. Hausen, loc. cit.

Finally, the specific volume  $v$  can be computed from  $\mu$  with the equation

$$\mu = \left( \frac{\partial T}{\partial p} \right)_h = \frac{T(\partial v / \partial T)_p - v}{c_p} = \frac{T^2 \left( \frac{\partial(v/T)}{\partial T} \right)_p}{c_p}. \quad (10)$$

For constant pressure this gives

$$d\left(\frac{v}{T}\right) = \frac{\mu c_p}{T^2} dT = \frac{\mu}{T^2} dh \quad (11)$$

and

$$\frac{v}{T} = \frac{v_0}{T_0} + \int_{T_0}^T \frac{\mu}{T^2} dh. \quad (12)$$

In this way all the thermodynamic properties can be determined and the

diagrams may be constructed. Figs. 80, 81 show the  $(h, T)$  and  $(T, s)$  diagrams of air, as computed by Hausen on the basis of his experiments.

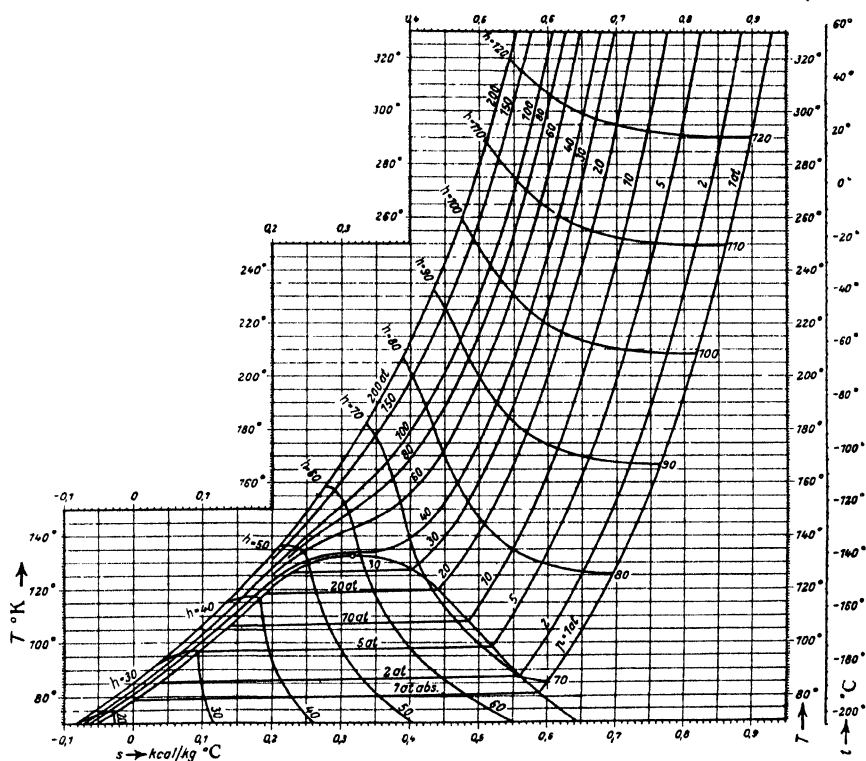


FIG. 81.  $(T, s)$  diagram of air. After H. Hausen, op. cit.

### 3. Refrigerating cycles

We can now answer the question as to how the performance of work and the delivery of heat may be so coordinated as to produce refrigeration. Suppose that we wish to cool a gas, say air, from room-temperature  $T_1$  to a low temperature  $T_2$ . The refrigerant is to be air itself and the pressure is to be atmospheric before and after the operation. From Fig. 81 we see that this requires a decrease in enthalpy and entropy of the air to be cooled, and from p. 106 we know that the work to be done is at least  $\Delta H - T_1 \Delta S$ .

The only way we can perform work on air is by compressing it. If we do this at constant room-temperature, making use of a heat reservoir at  $T_1$ , say water, we shall be delivering heat to this reservoir and simultaneously we shall be decreasing the enthalpy and entropy of the

air, as may be inferred from Fig. 82,  $AB$ . We can now perform one of the two following operations:

- (1) we can expand the air at constant enthalpy along the curve  $BC$ ;
- (2) we can expand it at constant entropy along  $BD$ .

The first operation may be carried out by allowing the air to expand in a throttle valve. This is a so-called Joule-Thomson expansion, in which  $H$  remains constant. It is characterized by the fact that, all

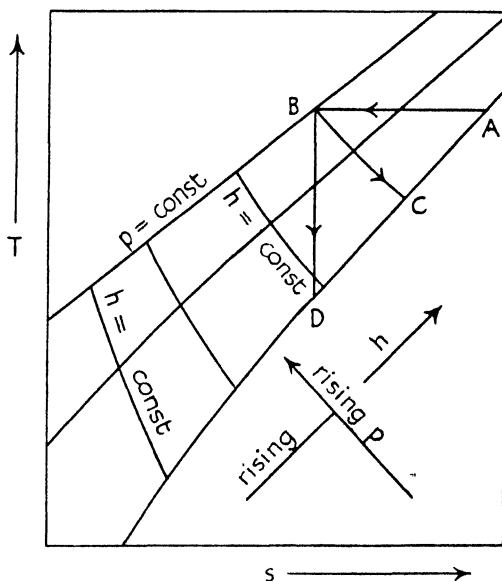


FIG. 82. Isothermal compression, isenthalpic expansion, and isentropic expansion on  $(T, s)$  diagram

through the expansion, the pressure on the low-pressure side of the valve is always atmospheric and thus much smaller than the momentary pressure on the high-pressure side, except right at the end of the expansion. The process is therefore irreversible, and the entropy increases. However, as Fig. 82 shows, the increase in entropy during the expansion is less than the decrease during the compression, so that finally the entropy of the air is less than at the commencement of the cycle. Since the enthalpy remains constant during the expansion, the total decrease in enthalpy is equal to that incurred during the compression. The air has passed through a refrigerating cycle, as a result of which its temperature, enthalpy, and entropy have been reduced. This cycle is called a *Linde* cycle, after Carl von Linde, who first used it to liquefy air in 1895. Strictly speaking, the cycle is, of course, incomplete, as the air, in its capacity of refrigerant, is not in

the same state afterwards as beforehand. This is because the same air, in its capacity of the object of refrigeration, has been cooled. This apparent confusion will be removed presently, when we shall see how the cycle is completed.

If the expanding air is made to move the piston of a reciprocating engine or the rotor of a turbine in such a way that the pressure it is operating against is always the same as, or very slightly less than, its own momentary pressure, the process is practically reversible, and so the entropy of the air will remain very nearly constant. On Fig. 82 the air will therefore move along the vertical line *BD*. In this case the entire reduction of entropy undergone by the air during compression will be maintained during the expansion, and, as we see from Fig. 82, the temperature and enthalpy will be reduced further than in the Linde cycle. This is known as the *Claude* cycle; it was first employed by Georges Claude to liquefy air in 1902. We see that the Claude cycle is apparently more potent than the Linde cycle, as its refrigerating performance is greater.

The Linde and Claude cycles were conceived in order to liquefy air with a view to its subsequent separation into oxygen and nitrogen. Neither of the operations described is in itself sufficient to cool the air to its point of condensation, still less to bring it into the liquid state. To do this, the process must be repeated in such a way that its refrigerating performance will be cumulative. This is effected with the help of a heat-exchanger. The introduction of the heat-exchanger is of vital importance in gas liquefaction; it is indeed the exchanger that makes the liquefier a refrigerator. When after expansion in the valve or cylinder the cold gas returns through the heat-exchanger, it is made to precool incoming warm gas. Here it plays the part of a refrigerant, in that it absorbs heat from the warm air. The transfer of heat takes place throughout the whole length of the heat-exchanger, out of which the expanded air emerges practically at room-temperature. In this way the entire refrigerating performance of the cycle remains inside the plant, the gas reappearing in the same state as it was in before compression. Only now is the cycle complete. The result is that the compressed air now reaches the valve or the cylinder at a lower temperature than before and, after expansion, its temperature is still lower. The temperature in front of and behind the valve or cylinder continues to fall until part of the air is liquefied in the course of the expansion.†

† In the Claude process liquefaction does not actually take place in the cylinder, but in an auxiliary cycle to be described later.



The liquefied air collects at the bottom of the apparatus and thereafter ceases to take part in the process; more especially, it no longer serves as a refrigerant. As the liquefied portion of the expanded air increases, the amount of refrigerant at our disposal decreases, until the refrigerating performance is no longer sufficient to lower the temperature any further. A stationary state is thus brought about, in which a certain fraction  $\epsilon$  of the incoming air is liquefied, the remainder  $(1-\epsilon)$  acting as refrigerant. After the stationary state has been attained the quantity and state of the air at all points of the plant remain the same and no longer depend on time, except in so far as liquid air is allowed to accumulate in the receiver.

During the stationary state of an air-liquefier a certain fraction  $(1-\epsilon)$  of the incoming air serves as a refrigerant, its function being to cool and liquefy the rest of the air. Before the stationary state is reached, all the air can be considered as refrigerant and its function is to cool itself. But since heat is nowhere withdrawn from the plant at a low temperature before the liquid is formed and drawn off, the refrigeration during the preliminary period is not apparent. It consists merely in lowering the temperature of the air in certain parts of the plant and of the metal tubes and vessels of which it is built. In the preliminary period we may say with equal justification that the air is cooling and that it is being cooled.

#### 4. The air liquefiers of Linde, Claude, and Heylandt

Linde and Claude are not the first pioneers of gas liquefaction. In 1877, eighteen years before Linde invented his cycle, small quantities of liquid oxygen were produced by Louis Cailletet in France and by Raoult Pictet in Switzerland. In the eighties all the then known permanent gases except hydrogen were liquefied regularly in Olszewski's laboratory at Crakow and the properties of the liquids were studied. In the early nineties Dewar was experimenting with liquid air in England and Kamerlingh Onnes was building his famous low-temperature laboratory at Leiden in Holland. Onnes's air-liquefier, which was based on the cascade principle, of which we shall have more to say later, was set up in 1892.

The great achievement of Linde is that he was the first to conceive the industrial implications of gas liquefaction and to put these ideas into practice. Linde realized that, through the liquefaction of gases, it would be possible to apply the well-known fractionating methods of the alcohol and petroleum industries to the separation of air, and so

to produce cheap oxygen. He foresaw that the production of liquid air on a commercial scale would be a profitable undertaking and would lead to the development of a new industry. Linde's apparatus was the first continuously operating engine, the first 'cycle', in the full sense of the word, for liquefying gases. Industrial gas liquefaction, and, in consequence, industrial gas separation, undoubtedly date from Linde's invention.

Several processes, the most famous of which were the Claude and Heylandt cycles, were developed shortly after the Linde liquefier appeared on the scene. All were subsequently combined with various separating units, for which they supplied the necessary refrigeration. In this section we shall consider air-liquefiers as such, distinct from their ulterior object of leading to the separation of air into its components.

In comparing various types of liquefier, it is best to determine the work required in each case to produce a certain quantity—say 1 gallon—of liquid air. This will give us a measure for the efficiency of a liquefier.

We shall find that, in every case, the work consists in compressing the air and, occasionally, some auxiliary gas, to a definite pressure. Moreover, in every liquefier only a part of the compressed air is actually liquefied, the rest returning through heat-exchangers and acting as a refrigerant. The fraction that is liquefied is known as the *coefficient of liquefaction* and denoted by  $\epsilon$ . Evidently, the greater  $\epsilon$ , the more efficient will be the liquefier, other things being equal. For to produce 1 gallon of liquid air, we must compress a quantity of air equivalent to 1 gallon of liquid divided by  $\epsilon$ . If  $\epsilon$  is very small, we must compress large quantities of air in order to obtain 1 gallon of liquid.

The work required to compress isothermally 1 mole of a perfect gas from a pressure  $p_2$  to a pressure  $p_1$  is equal to  $RT \log(p_1/p_2)$ , where  $R$  is the gas constant and  $T$  the absolute temperature. For air at room-temperature this expression is tolerably accurate up to moderately high pressures. The correct thermodynamic formula for the work required in compressing real gases is

$$W = \Delta H - T_0 \Delta S, \quad (13)$$

where  $\Delta H$  and  $\Delta S$  are the changes in enthalpy and entropy respectively incurred when the gas is compressed isothermally from  $p_2$  to  $p_1$  at a temperature  $T_0$ . Since thermodynamic diagrams have been constructed for air and for a number of other gases there is no difficulty in applying this formula.

There are two ways of defining the work needed to produce a gallon of liquid air with an apparatus of a given type. One is the work needed in theory on the assumptions that the compression is really isothermal and that there are no thermal and frictional losses. The other is the work actually needed in practice. Usually the latter is about twice as great as the former. To allow for frictional losses in the compressor and for the fact that the compression is never really isothermal but made up of a number of almost adiabatic stages, it is customary to multiply the theoretical work of compression by a factor of about 1.7. This figure is not very accurate as it will depend to a considerable extent on what type of compressor is used and especially on the number of stages. The thermal losses in the liquefier itself are caused by heat leakage through the lagging and by temperature heads at the warm ends of heat-exchangers, the expanding gases leaving the exchangers at a temperature lower than that of the environment. In well-constructed plants these temperature heads are usually about  $3^{\circ}\text{C}.$ ; when cold accumulators are used instead of exchangers they can be brought below  $2^{\circ}\text{C}.$  Heat leakage through the lagging is very serious in small liquefiers but far less important in large plants. In large-scale industrial apparatus it is roughly 0.3 B.Th.U. per cubic foot of gas (about  $2\frac{1}{2}$  kcal./cub. m.).

For calculations in this section we shall keep to the theoretical work of liquefaction, mentioning practical figures only occasionally for comparison. It should be pointed out that the theoretical work of liquefaction is quite distinct from the reversible work of liquefaction mentioned on p. 106. Whereas the latter is the minimum work needed in theory to produce a gallon of liquid air, using a fictitious reversible liquefier, i.e. the most efficient type of liquefier imaginable, the theoretical work of liquefaction is based on a certain type of liquefier, which in general involves irreversible processes, and merely assumes that this particular plant is perfectly lagged, cooled, and lubricated.

*Linde liquefiers.* We have already stated that the Linde liquefier is based on the isenthalpic expansion of compressed air. In its simplest form the plant consists of a compressor, a heat-exchanger, an expansion valve, and a vessel to collect the liquid. The liquefier is shown schematically in Fig. 83. Compressed air enters the heat-exchanger  $E$  at 1 and leaves it at 2. It is thereupon expanded in the valve  $V$ , so that, in the stationary state, it is partly liquid at 3. The liquid is drawn off at 4; the remaining vapour re-enters the heat-exchanger at 5 and finally leaves it at 6, after being warmed to almost room-temperature and so

precooling the incoming compressed air. The process is illustrated on the  $(T, s)$  diagram in Fig. 84.

To determine the coefficient of liquefaction  $\epsilon$ , consider the heat balance of the whole plant behind the compressor in the stationary

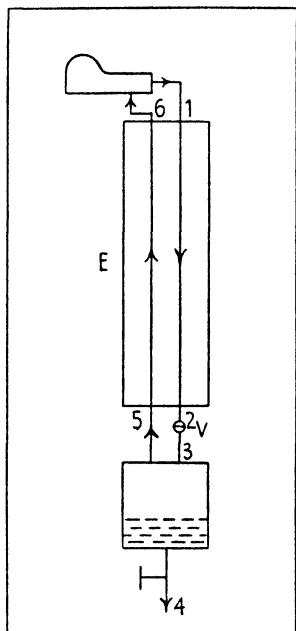


FIG. 83. Simple Linde liquefier

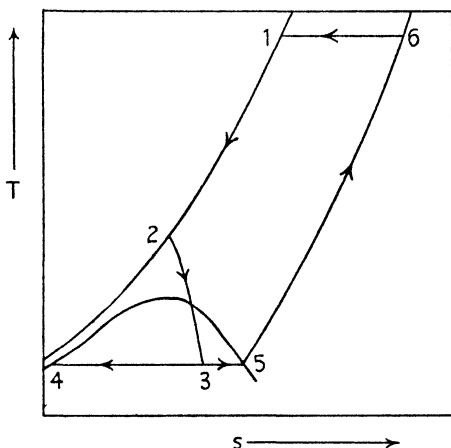


FIG. 84. Simple Linde cycle on  $(T, s)$  diagram

state. Suppose a certain quantity of air is introduced at 1 in a certain period of time. Then

$$H_1 = \epsilon H_4 + (1 - \epsilon) H_6,$$

so that

$$\epsilon = \frac{H_6 - H_1}{H_6 - H_4} = \frac{h_6 - h_1}{h_6 - h_4}. \quad (14)$$

Now  $h_4$  and  $h_6$  are the specific enthalpy of air as a saturated liquid and at room-temperature respectively, both at atmospheric pressure, and are thus material constants of air and independent of the nature of the plant. The only variable in the expression for  $\epsilon$  is  $h_1$ , which, at room-temperature, is a function of the pressure alone. Thus  $\epsilon$  depends merely on the pressure to which the air is compressed.

In order to liquefy 1 kg. of air, we must reduce its enthalpy from  $h_6$  to  $h_4$ .  $h_6 - h_4 = q$  is therefore the refrigerating performance required, and we can write

$$\epsilon q = h_6 - h_1. \quad (15)$$

On the other hand, liquefaction of 1 kg. requires that  $1/\epsilon$  kg. be sent

through the plant. The refrigerating performance of  $1/\epsilon$  kg. is therefore  $q$ , and that of 1 kg. is

$$\epsilon q = h_6 - h_1 = q'.$$

The work required may be computed from

$$W' = \Delta H' - T_0 \Delta S', \quad (16)$$

where  $\Delta H'$  and  $\Delta S'$  give the increase in enthalpy and entropy resulting from the compression of air from atmospheric pressure to the pressure used in liquefaction. Both quantities are negative. Using Hausen's  $(T, s)$  and  $(h, T)$  diagrams for air, in which  $h$  is given in kcal./kg. and  $s$  in kcal./kg. deg. C., we obtain the following data for working pressures of 50, 100, and 200 atm.

TABLE 12. *Simple Linde Liquefier*

$$h_4 = 22, \quad h_6 = 121, \quad s_6 = 0.893$$

$p_1$	50	100	200 atm.
$h_1$	117.5	114.8	111.1 kcal./kg.
$s_1$	0.630	0.580	0.518 kcal./kg. deg. C.
$\epsilon$	0.034	0.063	0.100
$w'$	0.0856	0.0983	0.116 kcal./kg. of compressed air
$w = w'/\epsilon$	2.52	1.56	1.16 kWh./kg. of liquid air
$w$	9.98	6.18	4.59 kWh./gallon of liquid air

We can evaluate the reversible work of liquefaction from

$$W_{\text{rev}} = \Delta H - T_0 \Delta S, \quad (17)$$

where  $\Delta H$  and  $\Delta S$  denote the difference between the enthalpy and entropy of liquid air boiling under atmospheric pressure and gaseous air at room-temperature and atmospheric pressure. With Hausen's data this gives

$$w_{\text{rev}} = 0.73 \text{ kWh./gallon of liquid air.}$$

If we take  $w_{\text{rev}}/w$  as a measure of the efficiency of the liquefier, we find that even the theoretical efficiency of a simple Linde liquefier, working at the relatively high pressure of 200 atm., is only 16 per cent. In practice the efficiency is not more than 8 per cent.

There are two ways of raising the efficiency of Linde liquefiers, both of which have been successfully applied. We may either seek to lower the work of compressing a given quantity of air, or we may try to raise the coefficient of liquefaction. At first sight the first suggestion may seem absurd, for it would apparently necessitate lowering the working pressure, and we have already seen that this leads to so great a decrease in  $\epsilon$  as far to outweigh the reduction in the work of compression. But there is another way of reducing this work: instead of lowering the high

pressure we can raise the low pressure. The liquefied air itself must, of course, be expanded to 1 atm., as it could not otherwise be tapped off, but we have seen that  $\epsilon$  is only a small fraction of the amount of air compressed. There is no necessity to expand the rest of the air to 1 atm. If we expand it to an intermediate pressure of some 40 atm., the refrigerating performance will be but slightly reduced, while the work of compression will be very much smaller. For it will mean that the greater part of the air passing through the plant will circulate merely between 40 and 200 atm. instead of between 1 and 200 atm. Since the work of compression is roughly proportional to  $\log(p_1/p_2)$ , compression from 40 to 200 atm. costs much less than compression from 1 to 40 atm. From our preceding discussion it is evident that this so-called *Linde high-pressure cycle* is characterized by a stronger differentiation between cooled air and cooling air than is the case in the simple liquefier. While the liquefied air is emitted at atmospheric pressure, most of the refrigerant is made to operate between a high pressure of 200 atm. and an intermediate pressure of about 40 atm.

The Linde high-pressure cycle is shown schematically in Fig. 85 and in diagram in Fig. 86. In the valve  $V_1$  the compressed air leaving the heat-exchanger is expanded to the intermediate pressure, and in  $V_2$  a certain portion  $\mu$  is further expanded to 1 atm., part being liquefied.  $(1-\mu)$  passes back through the exchanger at intermediate pressure via 4-5 and is readmitted to the highest stage of the compressor. The low-pressure side of the compressor takes in only as much air as is actually liquefied plus what emerges at 7.

The balance equation now reads

$$h_1 = (1-\mu)h_5 + (\mu-\epsilon)h_7 + \epsilon h_8,$$

which gives

$$\epsilon = \frac{h_5 - h_1 + \mu(h_7 - h_5)}{h_7 - h_8}. \quad (18)$$

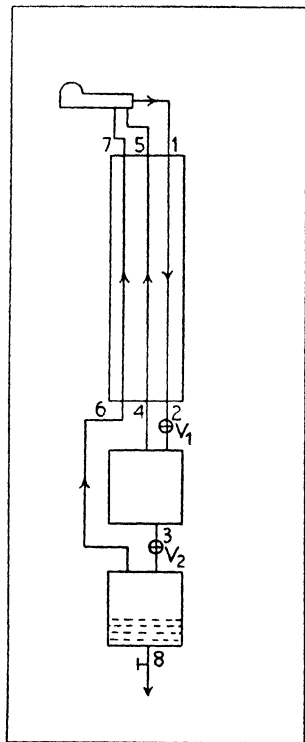


FIG. 85. Linde high-pressure cycle

The coefficient of liquefaction here depends not merely on the working pressure  $p_1$  but also on the intermediate pressure  $p_2$  and on the amount of air  $\mu$  expanded to 1 atm. The work needed also depends on these three independent variables. The calculations can again be made with the help of Hausen's diagrams. Fig. 87 shows the amount of work needed *in practice* to produce a gallon of liquid air by this method with

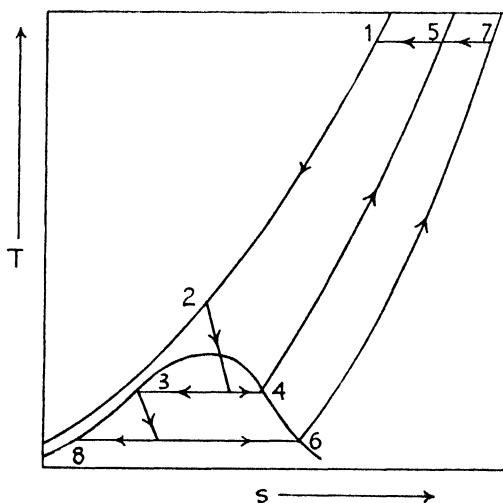


FIG. 86. Linde high-pressure cycle on  $(T, s)$  diagram. This diagram holds when the intermediate pressure is below the critical pressure of air (38.4 atm.). Otherwise points 3 and 4 coincide in a point outside the inhomogeneous region.

a working high pressure of 200 atm., as a function of the intermediate pressure  $p_2$ , for various values of  $\mu$ . The Linde plants usually work at  $\mu \sim 0.2$  and  $p_2$  from 40 to 50 atm. In this case  $\epsilon = 0.08$ , i.e. rather less than in the case of the simple liquefier, but the work of liquefaction is reduced to 3.23 kWh./gal. theoretically and about 6.0 kWh./gal. in practice.

The dotted line in Fig. 87 marks the limits up to which the high-pressure cycle can be applied. The existence of such limits can be inferred as follows. The Linde method is based on the fact that isenthalpic expansion of air leads to a fall in temperature, i.e. that the Joule-Thomson coefficient  $(\partial T / \partial p)_H > 0$ . It is as a result of this that the low temperature needed for liquefaction is actually attained. Later, in the stationary state, actual liquefaction, as we have seen, depends on the enthalpy difference between compressed and expanded

air at room-temperature, i.e. on  $\int_{p_2}^{p_1} (\partial H / \partial p)_T dp$ , but it is the positive sign of  $(\partial T / \partial p)_H$  that enables us to reach the low temperature and so to set up the stationary state to begin with. That is to say, that only such final states can be attained by the Linde method as can be reached from room-temperature through a complete series of intermediate states

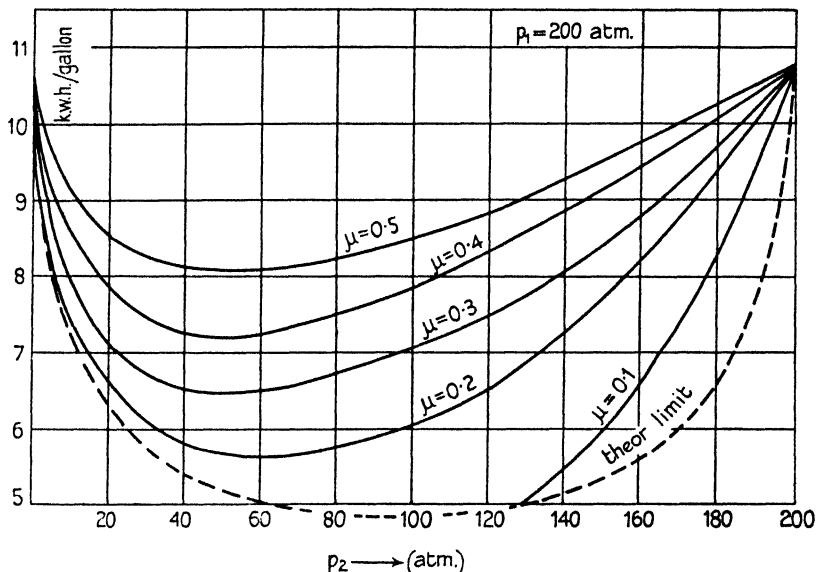


FIG. 87. Power consumption of Linde high-pressure cycle, working at 200 atm. high pressure, as a function of intermediate pressure for various amounts of gas expanded to 1 atm.

in which  $(\partial T / \partial p)_H > 0$ . Now at low temperatures and high pressures  $(\partial T / \partial p)_H$  becomes negative. This may be seen from Fig. 80, in which the lines of constant pressure intersect near the saturation curve at the bottom right-hand side of the figure. It is brought out more clearly in Fig. 88, which shows an exaggerated picture of the  $(h, T)$  diagram of air. The essential features are those of Fig. 80, but somewhat caricatured. We see that the point  $B$  in the upper part of the figure can be reached from  $A$  by means of isenthalpic expansion, starting at a higher temperature. But if we wanted to reach the point  $B'$  as a result of isenthalpic expansion, we should have to start from  $A'$ , which is at a lower temperature than  $B'$ , since in this region  $(\partial T / \partial p)_H$  is negative. And since, in the Linde method, the lowest momentary temperature in the apparatus has always been reached by isenthalpic expansion from a higher temperature, we may infer that the point  $B'$  is unattainable. Now if



we compute the temperature that must exist in the intermediate vessel in Fig. 85 in the stationary state, as a function of  $p_2$  and  $\mu$ , we find that, at points below the dotted curve in Fig. 87, the temperatures and pressures at this point of the plant would be unattainable. In order to

obtain a stationary state compatible with the balance equations, we must therefore keep within the region marked by the dotted line.

We have seen that there is, in principle, yet another method of raising the efficiency of the Linde liquefier, which consists in increasing the coefficient of liquefaction  $\epsilon$ . To achieve this, we must somehow raise the refrigerating performance of the cycle. A hint as to how this may be done can be obtained from studying the  $(T, s)$  diagram in Fig. 81. We see that the lines of constant enthalpy become steeper as the temperature falls. That is to say, that isothermal compression leads to a greater decrease in enthalpy, the lower the temperature. Now we can hardly compress air at a low temperature, but we can, quite easily and cheaply, precool the compressed air and so attain the same result. In the *Linde lique-*

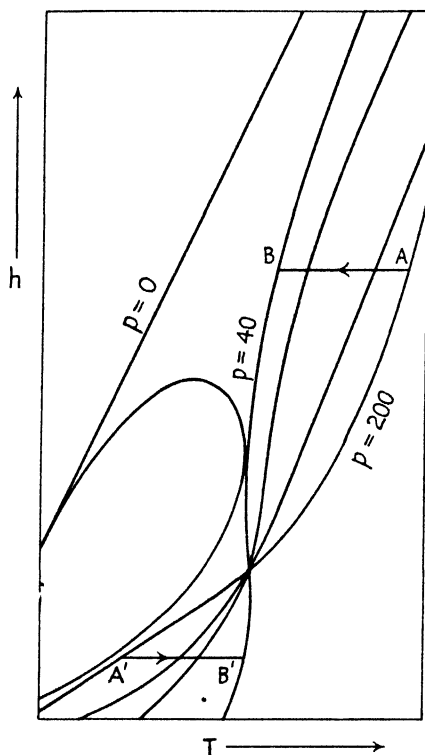


FIG. 88. Exaggerated  $(h, T)$  diagram, showing significance of limiting curve in Fig. 87

*fier with auxiliary ammonia cycle* the compressed air is precooled to about  $-45^{\circ}\text{C}$ . with liquid ammonia, boiling at reduced pressure. The ammonia refrigerator itself has a high refrigerating performance at this temperature. Thus the increase in  $\epsilon$  which it brings about outweighs the increased work of liquefaction due to the ammonia refrigerator, so that the total effect of the ammonia cycle is to reduce the amount of work needed to produce a gallon of liquid air. The ammonia cycle can be used with or without the high-pressure cycle. The lowest figure obtained for the theoretical work of liquefaction is  $1.91 \text{ kWh. per gallon}$ .

Comparative figures for the various types of Linde liquefiers are shown in Table 13.

TABLE 13. *Comparison of Linde Liquefiers*

	<i>Reversible process</i>	<i>Simple Linde</i>	<i>Linde with high pressure</i>	<i>Linde with ammonia cycle</i>	<i>Linde with high pressure and ammonia</i>
$\epsilon$	1.0	0.10	0.08	0.21	0.17
$w_{\text{theor}}$ (kWh./gallon)	0.73	4.59	3.23	..	1.91
$w_{\text{pract}}$ (kWh./gallon)	..	10.3	6.0	5.4	3.5

*Claude liquefiers.* The essential feature of the second type of air-liquefier, which is associated with the name of Claude, is the more or less isentropic expansion of compressed air in the cylinder of a reciprocating engine. In recent years these engines are gradually being replaced by turbines.† In no case, however, has a liquefier been based on this principle alone. Claude realized, as a result of his first experiments, that liquefaction in the cylinder itself is very inexpedient and, indeed, hardly possible. Not only is adiabatic expansion in itself very inefficient at temperatures and pressures near the critical point, but immense difficulties are encountered in lubricating the expansion engine at temperatures at which all known lubricants are solid bodies. After an ingenious attempt to lubricate the cylinder with liquid air, Claude resorted to a compromise, in which the expanded air in the cylinder is used to precool a separate cycle of air, the latter being thereupon expanded in a reducing valve and partially liquefied according to the Linde principle.

The apparatus is sketched in Fig. 89 and shown on the  $(T, s)$  diagram in Fig. 90. After passing through the first heat-exchanger,  $E_1$ , the compressed air separates. One part traverses the other two exchangers,  $E_2$  and  $E_3$ , is expanded in the valve  $V$ , and partially liquefied. The cold vapour returns through all three exchangers. The rest of the air (the refrigerant proper) is expanded in the cylinder  $C$  and joins the returning low-pressure air at 5. Since the expansion in the cylinder is never truly isentropic, the line 2-5 in Fig. 90 has been drawn slightly curved. Theoretically it should, of course, be a vertical straight line.

The liquefaction coefficient and power consumption of the Claude plant is a complicated function of a number of parameters: the initial pressure  $p_1$ , the fraction  $\mu$  of air passing through the valve, and the temperature  $T_2$  at which the rest of the air enters the cylinder. The deviation of the expansion in the cylinder from the isentropic line, and hence the temperature at which it leaves the expansion engine, is itself a function of the inlet temperature, as well as depending on the construction of the cylinder itself. There is little point in computing a

† See P. Kapitza, *Journal of Physics, U.S.S.R.* **1**, 7, 1939.

theoretical power consumption and we must hence rely on experimental figures.

It has been found empirically that, for each value of  $p_1$  and  $\mu$ , a definite temperature  $T_2$  exists which renders the power consumption a minimum. If we assume that, in every case,  $T_2$  is so chosen as to comply with this condition, we can plot the empirically determined power consumption as a function of  $\mu$  for various values of  $p_1$ . This has been done in Fig. 91. We see that each curve has a minimum at a certain value of  $\mu$ , but that this  $\mu$  increases and the height of the minimum decreases with rising pressure.

The conditions singled out by Claude correspond to the minimum of the curve for 40 atm. About 20 per cent. of the air is expanded in the valve and 80 per cent. passes through the cylinder. The most advantageous temperature at the intake is  $-80^\circ\text{C}.$ , and this condition is actually realized in Claude's liquefier, the power consumption of which is about *3.6 kWh. per gallon* and thus almost exactly the same as in the case of the Linde liquefier with high-pressure and ammonia cycles.

The power consumption at the minimum of the curve marked 200 atm. is *3.2 kWh. per gallon*, and the most economical intake temperature in this case has been found to be room-temperature.

These are the conditions of the *Heylandt* liquefier, which is now very frequently employed. It is the most efficient plant of this type; for by raising the pressure above 200 atm. we should simultaneously raise the most profitable intake temperature above that of the environment, a condition which would be hard to fulfil. The Heylandt liquefier has the advantage that it entails no difficulties in lubricating the cylinder. The air enters at room-temperature and leaves at about  $-125^\circ\text{C}.$ , at

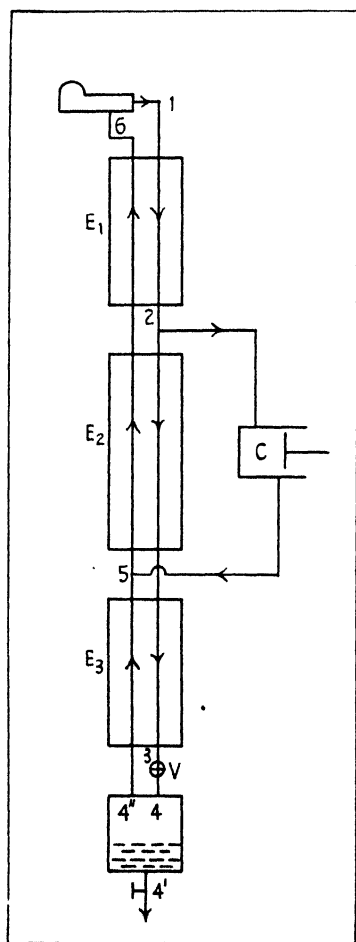


FIG. 89. Claude liquefier

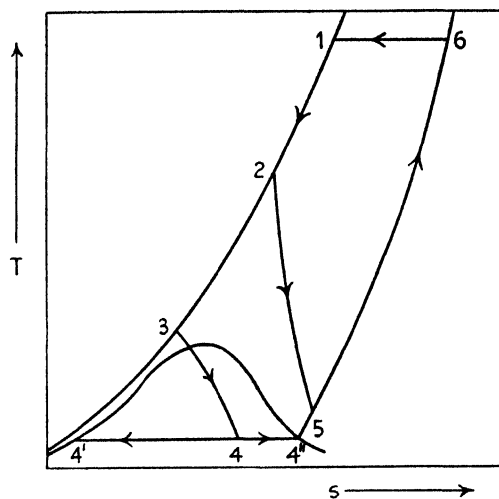
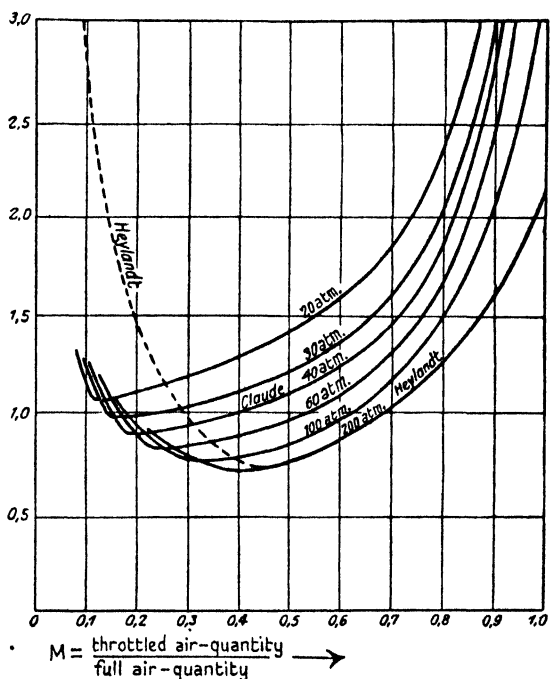
FIG. 90. Claude cycle on  $(T, s)$  diagram

FIG. 91. Power consumption in Claude and Heylandt liquefiers in kWh./kg. as a function of amount of air expanded in valve for various working pressures (1 gallon of liquid air weighs 4 kg.). After W. Lenz, *Handb. d. Exp. Phys.*, 9 (1929)

which light lubricants such as petroleum ether are quite satisfactory. The apparatus is further simplified in that the first heat-exchanger in Fig. 89 can be discarded.

In the Heylandt liquefier about 45 per cent. of the air is expanded in the valve and 55 per cent. passes through the expansion engine. Thus, whereas in the Claude plant the valve is a subsidiary appliance and the weight of the process is borne by the expansion engine, the weight of the Heylandt process is fairly evenly distributed between the two. The Heylandt plant, with its comparatively low power consumption, is a very clever synthesis of the principles of Claude and Linde.

The work performed by the air in the expansion cylinder can be utilized to lower the power consumption. The expansion engine is generally coupled with the compressor in such a way that the engine 'helps' the compressing motor. Though this help is not very considerable, it is by no means negligible. In the figures given above, this power economy has been taken into account.

### 5. The cascade principle and the analysis of losses

In commercial gas separation, especially when liquid products are required, the power consumption is a very important factor. This is due partly to the high reversible work of liquefaction and partly to the fact that very few hands are required to run a large-scale gas-separating plant, which tends to raise the relative cost of power as against salaries and wages. It is thus of primary importance to keep the power consumption as low as possible.

We have seen in the last section that the efficiency of air-liquefiers may be greatly improved by various devices and by altering the parameters of the plant. By introducing the high-pressure and ammonia cycles the efficiency of a Linde liquefier can be trebled, and a combination of the Linde and Claude principles offers a wealth of possibilities for varying the power consumption.

Yet to one not versed in the theory and technique of gas liquefaction the devices described may appear somewhat arbitrary. Though we have shown that, by precooling with liquid ammonia, the power consumption is, in fact, greatly reduced, in spite of the additional work consumed by the ammonia refrigerator, we may well ask why this is so, how we can gauge beforehand what effect a proposed alteration in the plant may have, and what type of alteration may be expected to bring advantages by reducing the power consumption.

We have seen that the minimum amount of work needed to liquefy a quantity of gas is the so-called reversible work of liquefaction

$$W_{\text{rev}} = \Delta H - T_0 \Delta S,$$

which is, of course, merely a function of the properties of the gas to

be liquefied and independent of how the refrigeration is carried out. To bring about the necessary reduction in the enthalpy and entropy of the air, we employ a refrigerant, which may or may not be air itself, and on which a certain amount of work  $W$  is performed. As we have seen,  $W$  is always considerably greater than  $W_{\text{rev}}$ . Now if  $W_{\text{rev}}$  is sufficient in theory to produce a given quantity of liquid air, how does it come about that an amount of work equal to  $W_{\text{rev}}$  does not, in practice, produce the effect that it should? The reason can only be that the refrigerating cycle is not a reversible process. For  $W_{\text{rev}}$  must be independent of how the work is applied, as long as it is reversible. Therefore the question whether a certain type of liquefier is more or less efficient than another reduces to the question whether it is less or more irreversible. Again, as in the preceding chapter, we need a measure of irreversibility.

We already know that this measure is to be found in the changes of entropy undergone within the plant in the stationary state. If we take an entropy balance of the plant as a whole, we find that the sum of the entropies of all substances emerging is always greater than that of all substances entering. The difference of these two sums is a direct measure of the irreversibility of the process. Moreover, the total increase in entropy of the plant as a whole is equal to the sum of the entropy increments incurred in all its individual parts. We can thus find out what role a given operation, conducted within the apparatus, is playing in increasing the entropy and thus in increasing  $W$ . As we saw in our discussion of separation processes, every increase in entropy  $\Delta S$  necessitates the expenditure of work to the amount of  $T_0 \Delta S$  in addition to  $W_{\text{rev}}$ , where  $T_0$  is room-temperature, i.e. the temperature at which the work must be performed.

Now in every refrigerating cycle a certain irreversible increase of entropy occurs and this must be compensated by additional work. But the only way this work can be performed is by passing more refrigerant through the plant. This entails a further increase in entropy, since the cycle is irreversible, and for this compensation must again be made, and so on. Thus, if every pound of refrigerant passed through the plant and involving an expenditure of work  $w^*$  is accompanied by an irreversible increase of entropy  $\Delta s_{\text{irr}}^*$ , only the amount  $w^* - T_0 \Delta s_{\text{irr}}^* = w_{\text{rev}}^*$  is really useful work. If  $m$  pounds of refrigerant would be needed to produce a gallon of liquid air in a reversible process, involving the expenditure of an amount of work  $W_{\text{rev}}$ , then

$$W_{\text{rev}} = mw_{\text{rev}}^*. \quad (19)$$

But in order to produce the gallon of air with  $m$  pounds of refrigerant in our irreversible process, we should have to perform more work on that refrigerant, and the total amount of work performed would be

$$W = mw^* = m(w_{\text{rev}}^* + T_0 \Delta s_{\text{irr}}^*) = m(w_{\text{rev}}^* + w_{\text{irr}}^*). \quad (20)$$

Now, instead of performing more work on the refrigerant, we want to pass more refrigerant through the plant, so that the work done on each pound of refrigerant is still  $w_{\text{rev}}^*$ . Then the amount  $M$  of refrigerant needed is given by the relation

$$Mw_{\text{rev}} = m(w_{\text{rev}}^* + w_{\text{irr}}^*).$$

Hence

$$M = m(1 + w_{\text{irr}}^*/w_{\text{rev}}^*). \quad (21)$$

To find out what type of liquefier is the most efficient we must first know where entropy changes are likely to occur in liquefiers. We shall here neglect the entropy increases in compressors and confine ourselves to the low-temperature plant itself.

Irreversible changes will occur wherever gases having different temperatures are brought into thermal contact, i.e. in all heat-exchangers and in evaporators and condensers. For there must always be a temperature head where heat is transferred. These sources of entropy increase are generally small compared with those occurring in throttle valves. We have already shown that this form of expansion is irreversible and it will become apparent that the irreversibility is indeed very serious. But we must now show that the irreversible entropy changes incurred during isenthalpic expansion vary greatly according to the temperature at which the air is expanded. Let us take the expansion of air from 200 to 1 atm., starting at various temperatures. The accompanying entropy increments are shown in the following table:

TABLE 14. *Increase in Entropy in kcal./kg. degree C. during the Isenthalpic Expansion of Air from 200 atm. to 1 atm.*

$T$ ( $^{\circ}$ abs.)	$s_{200}$	$s_1$	$\Delta s$
320	0.54	0.90	0.36
260	0.47 <sub>5</sub>	0.82	0.34 <sub>5</sub>
205	0.39	0.69	0.30
160	0.28	0.48	0.20
115	0.14	0.22 <sub>5</sub>	0.08 <sub>5</sub>

The first three expansions take place wholly in the gaseous phase, the fourth leads to partial liquefaction, the fifth is the expansion of a super-

cooled liquid leading to partial evaporation. Clearly  $\Delta s$  decreases as the initial temperature falls, and the farther we proceed into the liquid phase the smaller  $\Delta s$  becomes. The isenthalpic expansion of a liquid is far less irreversible than that of a gas.

This fact is very important as it shows us what line to take in order to raise the efficiency of liquefiers. For one thing it explains the advantage obtained from the ammonia cycle. The introduction of the ammonia refrigerant reduces the necessary quantity of refrigerating air, thus lowering the temperature in front of the expansion valve, decreasing the entropy change during expansion, and increasing the coefficient of liquefaction. In the ammonia refrigerator itself the entropy increments are small, since the ammonia is expanded as a liquid. The irreversibility of the plant as a whole is therefore less than in the case of the simple Linde cycle, and so the power consumption is smaller.

But the principle we have just discussed enables us to go much farther in improving the efficiency of liquefiers. Recognizing that expansion of a liquid is more economical than expansion of a gas, we may construct a liquefier in which only liquids are expanded. Air itself cannot be liquefied in liquid ammonia, even if the latter boils at a low pressure. But we can find a series of gases, with progressively falling boiling-points, each of which may be liquefied under pressure in the condensed phase of the one before it. This is the well-known *cascade principle*, first conceived by Pictet and later carried out by Kamerlingh Onnes and treated theoretically by Keesom.

Keesom's† proposed cascade for liquefying nitrogen contains four cycles: ammonia, ethylene, methane, and nitrogen. The ammonia is liquefied at room-temperature and 10 atm. pressure and the liquid expanded. Ethylene is liquefied at 19 atm. in liquid ammonia, methane at 25 atm. in liquid ethylene, boiling at atmospheric pressure, and finally nitrogen is liquefied in liquid methane at 18.6 atm. This rather complicated apparatus is shown schematically in Fig. 92. It is characterized by the fact that only liquids are expanded. According to Keesom's calculations, the efficiency of this plant should be much greater than that of any of those hitherto described. Including all probable losses, Keesom computes a 'practical' power consumption of only 2.04 kWh. per gallon of liquid nitrogen. The results of Keesom's calculation are set forth in Tables 15 and 16. Table 17 shows the irreversible entropy increments in the various units of the plant.

† W. H. Keesom, *Leiden Commn.*, Suppl. No. 76a.



TABLE 15. *Keesom's Nitrogen Cascade*

$m$ (kg.)	No.	$p$ (atm.)	$T$ (°C.)	$f$ †	$h$ (kcal./kg.)	$s$ (kcal./kg.°C.)
NH <sub>3</sub> 0.331	a	10.2	25	..	128.0	1.097
	b	1.0	-34	0.196	128.0	1.128
	c	1.0	-34	1.000	390.8	2.224
	d	1.0	17	..	417.7	2.332
C <sub>2</sub> H <sub>4</sub> 0.963	e	19.0	25	..	74.2	0.312
	f	19.0	-7	..	64.9	0.275
	g	19.0	-31	0.000	-25.5	-0.093
	h	1.0	-104	0.341	-25.5	-0.052
	i	1.0	-104	1.000	44.0	0.361
	j	1.0	17	..	79.3	0.517
CH <sub>4</sub> 0.660 (0.636 through $E_3$ , 0.024 through $E_2$ )	k	24.7	25	..	220.4	1.254
	l	24.7	-75.9	..	165.7	1.047
	m	24.7	-101.0	0.000	64.3	0.463
	n	1.0	-161.6	0.447	64.3	0.582
	o	1.0	-161.6	1.000	132.6	1.195
	p	1.0	17	..	221.0	1.647
N <sub>2</sub> 1.770  1.000 0.770	q	18.6	25	..	108.9	0.827
	r	18.6	-158.6	0.872	52.6	0.522
	s	18.6	-168.6	0.000	27.1	0.301
	t	1.0	-195.8	0.435	27.1	0.363
	u	1.0	-195.8	0.000	6.7	0.100
	v	1.0	-195.8	1.000	53.65	0.707
	w	1.0	17	..	110.0	1.056

†  $f$  for inhomogeneous phases denotes *quality*, i.e. the ratio of the amount of gas to the total amount of substance present.

TABLE 16. *Keesom's Nitrogen Cascade*

*Thermal Equivalent of Work needed per kg. of Liquid Nitrogen*

Compressor	Kcal.
NH <sub>3</sub> . . .	25.6
C <sub>2</sub> H <sub>4</sub> . . .	52.9
CH <sub>4</sub> . . .	76.3
N <sub>2</sub> . . .	117.7
	<u>272.5</u>

Effective work:  $272.5 \times 1.7 = 463$  kcal.  
 $= 0.539$  kWh./kg.  
 $= 2.04$  kWh./gallon.

The total work, calculated as the sum of the irreversible and reversible work in Table 17, is seen to be equal to the sum of the work done by the four compressors, as shown in Table 16, within the error of calculation. Here the losses in the compressors themselves must, of course, be excluded.

TABLE 17. *Keesom's Nitrogen Cascade**Analysis of Losses*

Part	$T_0 \Delta s$ (kcal./kg.)
$R_1$ . . .	3.0
$V_1$ . . .	2.2
$E_1$ . . .	0.5
$R_2$ . . .	11.7
$V_2$ . . .	3.7
$E_2$ . . .	7.3
$R_3$ . . .	23.4
$V_3$ . . .	4.0
$E_3$ . . .	4.9
$R_4$ . . .	32.7
Irreversible work . . .	93.4
Reversible work (theor.)	182.9
Total work	276.3

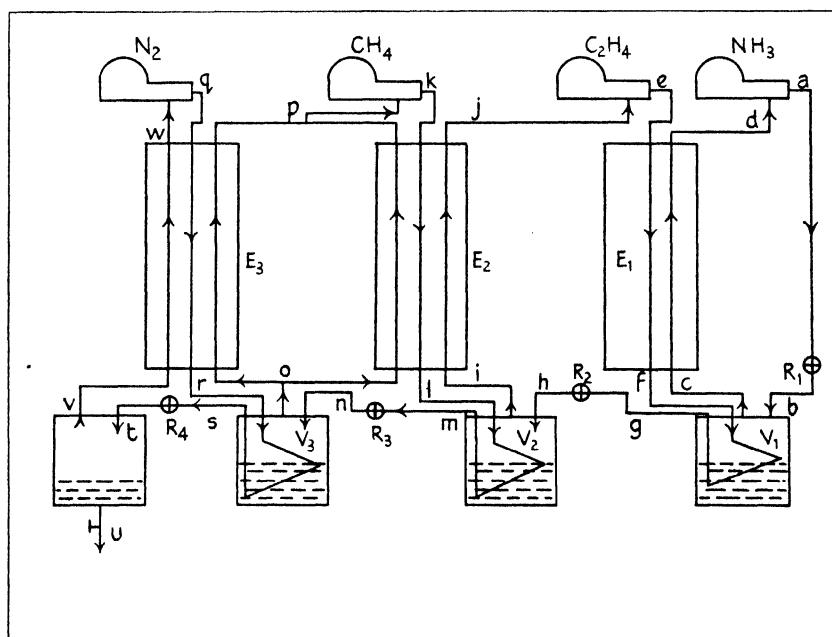


FIG. 92. Keesom's nitrogen cascade

Summing up the results of our discussion, we come to the following conclusions:

1. The efficiency of a liquefier, as defined by the ratio of the reversible work of liquefaction to the actual power consumption, depends on the irreversible entropy increments occurring at various points in

the plant. Each irreversible entropy increment  $\Delta S$  leads to an additional power consumption  $T_0 \Delta S$ , where  $T_0$  is room-temperature.

2. The principal sources of such irreversible entropy increase are to be found in the isenthalpic expansion of gases and, to a lesser degree, in heat transfer between gases of widely differing temperatures at the cold ends of heat-exchangers.
3. The lower the temperature of the compressed gas before its isenthalpic expansion, i.e. the nearer it is to a state of saturation, the smaller are the irreversible entropy changes involved.
4. The entropy increase occurring during the expansion of a liquid (in the course of which a part evaporates) is much smaller than in the case of a gas.
5. The low degree of irreversibility, coupled with increased refrigerating performance, makes it profitable, wherever possible, to employ refrigerants near a state of saturation.
6. The cascade system of liquefaction, an example of which was given above, constitutes a logical application of these arguments.

## VI

### THE SEPARATION OF AIR (1)

#### AIR AS A BINARY MIXTURE

##### 1. The simple column

IN this chapter we shall regard air as a binary mixture, consisting of 79.1 per cent. nitrogen and 20.9 per cent. oxygen. We shall assume that moisture and carbon dioxide have been removed before the air enters the plant and we shall neglect the presence of rare gases. The considerable part that argon plays in the separation of air will be treated in Chapter IX.

The simple still or rectifying column is the prototype of all apparatus for separating air. Though it has long been superseded by more elaborate designs, it offers a convenient starting-point for discussion, combining as it does almost all the elements of construction that occur in subsequent improved columns with historical precedence and clarity of principle.

Fig. 93 shows the original plant patented by Linde in 1902. Compressed air is introduced at *B* through the heat-exchanger *H*, traverses a number of turns of copper tubing in the evaporator or sump *E*, and is expanded to atmospheric pressure in the valve *V*, whereupon it is delivered at the top of the column in the liquid state. The liquid falls from plate to plate and is partially or wholly evaporated at the bottom of the column by means of the compressed air passing through the coil. In the stationary state oxygen collects in the sump, whence either liquid or the vapour rising therefrom may be continuously withdrawn. Impure nitrogen vapour emerges at the top of the column and the gaseous products are removed through *H*, cooling the incoming air. The gaseous oxygen, which can be made as pure as we desire, is collected in a gas-holder, and the nitrogen, which is always impure, is usually emitted to the atmosphere.

While the apparatus is being cooled down it must, of course, work as a refrigerator. If liquid oxygen is to be produced, the same is true in the stationary state. If only gaseous products are required, refrigeration is needed only to compensate for heat leakage through the lagging surrounding the column.

In order that a stationary state may be maintained, in which oxygen of required purity is continuously produced, certain conditions must be fulfilled as regards construction and régime of the column. Many

methods have been suggested to compute the data needed to determine these conditions, but most of these aim at determining only certain particular properties of columns. We shall here follow the line taken by Keesom,<sup>†</sup> as it enables us in principle to obtain almost all the quantities in a single series of operations.

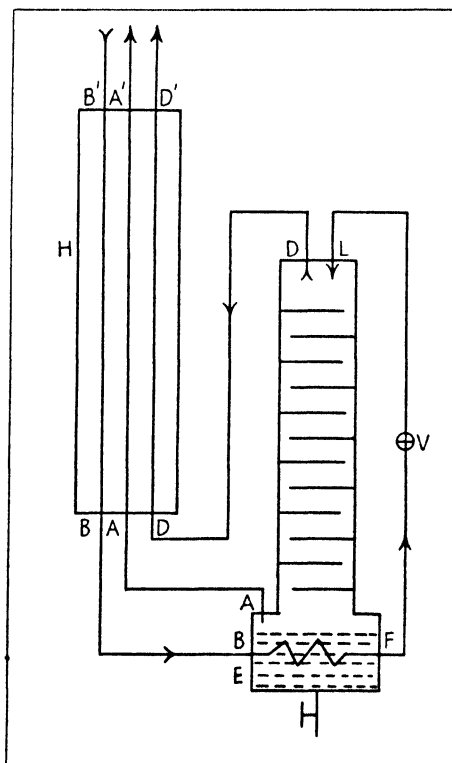


FIG. 93. Simple Linde air column

According to Keesom, we can find out everything of interest about an apparatus for separating gases if at certain characteristic points we determine the following quantities:

1. Amount of matter passing in a given time.
2. Composition.
3. Temperature.
4. Pressure.
5. Specific enthalpy.
6. Specific entropy.

<sup>†</sup> W. H. Keesom, *Actes du VI<sup>ème</sup> Congrès International du Froid*, Buenos Aires, 1932: *Rapport de la 1<sup>ère</sup> commission*, p. 136.

The characteristic points may, to a certain extent, be chosen arbitrarily and their total number will depend on the extent of detail that we desire to elucidate. As a rule, the points are profitably chosen between the individual parts of the apparatus. A number of the values needed are given directly by the size and requirements of the plant; others may be read off from existing thermodynamic diagrams. The

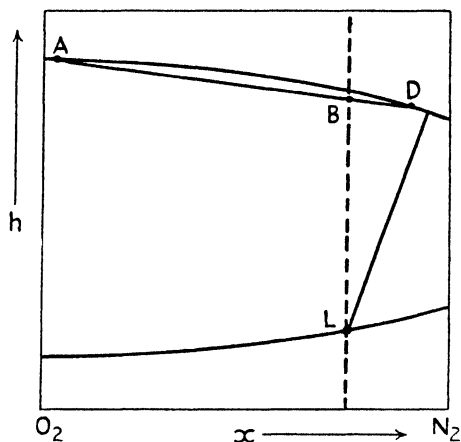


FIG. 94. Representation of simple air column on  $(h, x)$  diagram

rest may be found graphically with the help of simple constructions or analytically by solving certain balance equations. In our first calculations we shall leave entropy out of account and confine ourselves to the other data.

*Representation on the  $(h, x)$  diagram.* First let us consider the column alone without the heat-exchanger. Suppose that we wish to obtain gaseous oxygen at  $A$  (Fig. 93) of a degree of purity  $x_A$ . The nitrogen product emerges at  $D$  and liquid air is introduced at  $L$ . The compressed air enters the evaporator coil at  $B$  and leaves it at  $F$ . To begin with we may neglect heat losses and suppose the column to be adiabatic. We assume that it works at atmospheric pressure.

Now let us turn to the  $(h, x)$  diagram of oxygen–nitrogen mixtures, which is shown schematically in Fig. 94. Since the air at  $L$  is boiling and has atmospheric composition, we can plot point  $L$  as the intersection of the liquid branch and the ordinate for  $x = 0.79$ . Similarly, we can plot  $A$  as a saturated vapour of the specified composition (say 99 per cent.  $O_2$ ).

To determine the position of  $D$ , consider the top plate (Fig. 93). The liquid  $L$  enters this plate from above and a liquid  $L'\dagger$  leaves it below.

† Not shown in the figure.

The vapour  $D$  which leaves the plate will at the best be in equilibrium with  $L'$ . But  $L'$  contains more oxygen than  $L$ . Therefore  $D$  will contain more oxygen than a vapour in equilibrium with  $L$ . From the equilibrium curves of oxygen-nitrogen mixtures, which appear in the connodals of the  $(h, x)$  diagram, we know that a vapour in equilibrium with liquid atmospheric air (79.1 per cent.  $N_2$ ) contains 93.5 per cent.  $N_2$ . This is therefore the upper limit for the nitrogen content of  $D$ . It will soon become apparent that below this limit  $x_D$  may be chosen arbitrarily. For the present we shall put  $x_D = 91$  per cent.  $N_2$ .

Now consider the balance equation of the column as a whole. Since we have assumed the apparatus to be adiabatic, we have

$$B = A + D. \quad (1)$$

But  $x_B = 0.79$ . So  $B$  is on the straight line through  $A$  and  $D$  at its point of intersection with the ordinate  $x = 0.79$ .

Now since  $F$  passes into  $L$  by means of an expansion in a valve, in the course of which the enthalpy remains unchanged,  $h_L = h_F$ , and as mass and composition are not altered by expansion, we can put, as far as the  $(h, x)$  diagram is concerned,  $L = F$ .

If  $Q$  is the amount of heat transferred to the evaporator from the compressed air passing through the coil, we have

$$L + Q = A + D = B,$$

or

$$Q = B - L. \quad (2)$$

From our definition of equation (16), p. 95, we thus have

$$Q = m_B(h_B - h_L) = m_B(BL),$$

where  $BL$  is the length of the straight line joining  $B$  and  $L$ .  $BL$  is therefore the amount of heat exchanged in the evaporator per unit mass of air passing through the plant.

If the heat leakage cannot be neglected, we must take into account an amount of heat  $Q'$  which passes in the given time through the insulation of the column. Equation (1) must then be written

$$B = A + D - Q'.$$

The point  $B$  will therefore be lower on the figure by an amount  $Q'/m_B$ .

Now consider the heat-exchanger (Fig. 93). If the heat leakage may be neglected, we have

$$B' + D + A = B + A' + D'. \quad (3)$$

If an amount of heat  $Q''$  leaks into the exchanger, the balance equation reads

$$B' - B = A' - A + D' - D - Q''. \quad (4)$$

In this equation  $Q''$  is given,  $A$  and  $D$  are known from the diagram, and  $A'$  and  $D'$  may also be determined from the diagram since they refer to 1 atmosphere and room-temperature. We may for the moment assume that the exchanger is long enough to ensure complete exchange, so that the gases emerge at the same temperature as  $B'$ . As for  $B$ , we know its mass, composition, and enthalpy but not its temperature and pressure.

Now from equation (4) we can determine the enthalpy of  $B'$ , and since we know its temperature we can find the pressure from an  $(h, T)$  or  $(T, s)$  diagram of atmospheric air. But this pressure is the same as that of  $B$ . The same diagram will therefore give us the temperature of  $B$ , whereupon all the data are known that concern the plant as a whole. In case a difference in temperature must be taken into account between the gases entering and leaving the warm end of the exchanger, the values of  $h_A$  and  $h_{D'}$  must be correspondingly reduced.

The work required to effect separation is consumed in compressing atmospheric air from 1 atmosphere to the pressure of  $B'$ . For isothermal compression of a perfect gas, this is

$$A = nRT \log p_{B'}/p_0,$$

where  $p_0 = 1$  atm. For air at room-temperature this is approximately correct. We have seen how a more accurate value may be obtained. In practice the work will be greater, as the compression is never strictly isothermal and the efficiency of the compressor less than unity.

**EXAMPLE.** 3,000 cub. ft. of air per hour are to be separated at 1 atm. into gaseous components containing 98 per cent. oxygen and 91 per cent. nitrogen respectively. The heat leakages amount to 0.3 B.T.U. per cub. ft., of which 0.2 are lost in the column and 0.1 in the heat-exchanger. To what pressure must the air be compressed? What is the temperature of the compressed air leaving the exchanger? How much heat is exchanged in the evaporator?

Let the letters  $A, A', B, B', D, D', L, Q, Q', Q''$  have the same meaning as above. From the data given we may write down directly the values of the following:

$$m_B = m_L, \quad x_B = x_L, \quad x_A, \quad x_D, \quad T_{B'} = T_{A'} = T_{D'}, \quad Q', \quad Q''.$$

From the  $(h, x)$  diagram we obtain without further construction

$$h_L, \quad h_A, \quad h_D.$$

By subtracting  $Q'/m_B$  from the point of intersection of  $AD$  and the



ordinate  $x = 0.79$  we obtain  $h_B$ .  $BL$  multiplied by  $m_B$  then gives  $Q$ . From the balance equations of mass and composition

$$m_A + m_D = m_B,$$

$$x_A m_A + x_D m_D = x_B m_B,$$

we find  $m_A$  and  $m_D$ .

The balance equation of the heat-exchanger

$$B' = B + A' - A + D' - D - Q''$$

gives us  $h_{B'}$ . Since  $T_{B'} = 290^\circ \text{K.}$ , we find  $p_{B'}$  from the  $(T, s)$  diagram of air. Knowing  $p_B$  and  $h_B$ , we determine  $T_B$  from the same diagram.

The numerical data are given in Table 18.

TABLE 18. Numerical Data for the Separation of 3,000 cub. ft. of Air per hour into 98 per cent.  $\text{O}_2$  and 91 per cent.  $\text{N}_2$  in a Simple Column

Point	$m$ , cub. ft.	$p$ , atm.	$T$ , $^\circ\text{K.}$	$x$ , mole % $\text{N}_2$	$h$ , cal./mole
$B$	3,000	33	130	79	1,618
$A$	400	1	90	2	1,732
$D$	2,600	1	78	91	1,655
$L$	3,000	1	79	79	258
$B'$	3,400	33	290	79	3,058
$A'$	400	1	290	2	3,112
$D'$	2,600	1	290	91	3,131

$$Q = 4,845 \text{ kcal./hr.}$$

If liquid oxygen is to be produced we have less cold gas to precool the air in the exchanger and greater refrigeration is needed than if only heat losses need be covered. Accordingly it will be necessary to compress the air to a higher pressure.

*Determination of the number of plates required.* The preceding discussion has enabled us to adjust the régime of our column after a stationary state has been reached. However, we have not as yet inquired whether this stationary state can in fact be attained. While the apparatus is being cooled a greater refrigerating performance is needed, and this may be obtained by raising the pressure of the air during this period. But we must now find out how the plant must be constructed to produce pure oxygen. Not every plate column will achieve this. We must determine how many plates are needed to secure a certain degree of purity. This is one of the most subtle questions of gas separation and it has been solved only as a result of several successive approximations. At this early stage of the discussion we shall keep to the first approximation.

We shall assume that vapour and liquid actually attain equilibrium on every plate, so that a liquid leaving a plate is in equilibrium with the vapour rising from the same plate, and we shall suppose that between the plates no interaction occurs between vapour and liquid. Moreover, we assume that the composition of the liquid is the same throughout the plate.

In Chapter IV we introduced the concept of equivalent current as the difference between the liquid and the vapour phase in a section of a separator, and we showed that the equivalent current is a constant throughout the apparatus. Thus, if  $L_n$  and  $G_n$  are the liquid and gaseous phases passing a section above the  $n$ th plate, we can write the equations

$$L-D = L_1-G_1 = L_2-G_2 = L_n-G_n = \dots = Z.$$

But the balance of the column as a whole (Fig. 93) gives

$$L-D = A-Q,$$

so that

$$Z = A-Q,$$

which means that  $x_Z = x_A$ . So we can plot  $Z$  as the point of intersection of the straight line  $LD$  and the ordinate through  $A$ , and all the straight lines  $L_n G_n$  will pass through  $Z$  (see Fig. 95).

Now  $D$  is the gas leaving the top plate. According to our assumption, the liquid  $L_2$  leaving the first plate will be in equilibrium with  $G_1 = D$ . So on the  $(h, x)$  diagram we can plot  $L_2$  as the lower end of the connodal through  $D$ . If we now join  $ZL_2$  and produce to the vapour curve, the point of intersection will give  $G_2$ , and  $L_3$  is the lower end of the connodal through  $G_2$ . Evidently this operation can be continued until some vapour phase  $G_n$  coincides with or passes  $A$ . The number of steps is equal to the number of plates needed.

We see at once that this construction is feasible only if the slopes of the lines  $ZL_n G_n$  are steeper than the connodals. If a connodal coincided with one of these lines we should not be able to move across the figure. More especially, if  $LD$  coincided with the connodal through  $L$  we should be unable to start. This brings out very clearly the fact, already noted, that  $D$  must contain less nitrogen than is in equilibrium with  $L$ .

Moreover, the steeper  $LD$  is, compared with the connodal through  $L$ , i.e. the impurer the nitrogen product, the farther the first and every subsequent step will take us in the direction of  $A$ . That is to say, the fewer plates will be needed to obtain a given degree of oxygen purity. If the number of plates is less than that found graphically by this

method, we shall not be able to obtain oxygen of the desired concentration without making the nitrogen impurer than was stipulated.

*Reversible and irreversible work of separation.* The work  $W$  of separating air into pure oxygen and impure nitrogen is simply the work of compressing the air to the required pressure, and this, as we have seen, is given by the conditions of the plant.  $W$  is usually very much greater

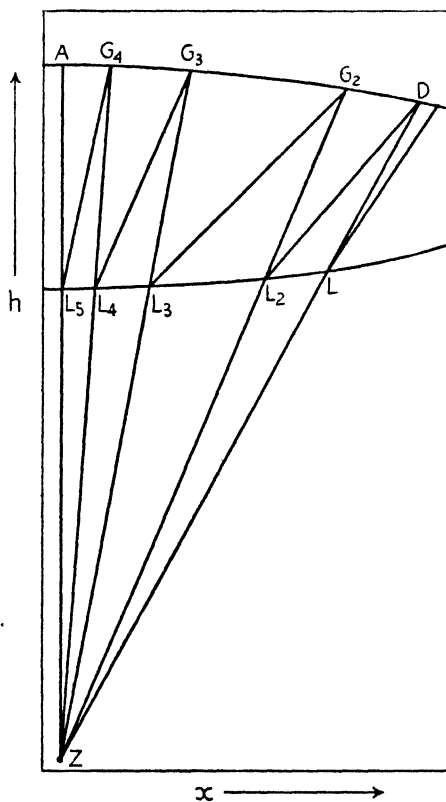


FIG. 95. Determination of number of plates in simple column

than the theoretical work  $W_{\text{rev}}$ , which would be needed if the process were completely reversible and which may be computed from formula (22) on p. 104. Part of this discrepancy is due to the low efficiency of the compressor and to the fact that the compression is in reality not isothermal but almost adiabatic. In practice the work done by the compressor is from 1.6 to 1.7 times as great as it would be for the case of isothermal compression and an efficiency equal to unity. But this only covers a small fraction of the difference between  $W_{\text{rev}}$  and  $W$ .

A further source of additional work is due to the heat leakage into the column and exchanger from the environment. This heat leakage, as we have seen, requires refrigeration so that the stationary state may be maintained, and refrigeration demands work. The removal of an amount of heat  $Q_0$  at a temperature  $T_0$  and its disposal at a temperature  $T_1 > T_0$  necessitates the consumption of an amount of work  $W'$ , so that

$$W' \geq Q_0 \frac{T_1 - T_0}{T_0}.$$

An accurate calculation of  $W'$  is complicated by the fact that the heat  $Q$  is imparted to the apparatus throughout its whole extent, that is to say, at various temperatures. However, we can usually obtain a fair approximation by separating  $Q$  into two parts, as was done above, and assuming one part to enter the column and the other the exchanger. In the case of air the difference in temperature between the top and bottom of the column is small compared with that between the column and the environment, so that we shall not go far wrong in taking the mean temperature of the column as a whole. In taking the mean temperature of the exchanger we must remember that the heat flux per unit surface is the greater the lower the temperature.

But there is yet another source of work, and this is due to irreversible changes occurring within the column. In Chapter IV we showed that such a change, which leads to an increase in entropy  $\Delta S_{\text{irr}}$ , requires the expenditure of an amount of work equal to  $T_0 \Delta S_{\text{irr}}$ , where  $T_0$  is the temperature of the surroundings, in our case room-temperature, at which this work must be performed. Moreover, we pointed out how  $\Delta S_{\text{irr}}$  may be determined graphically with the help of the  $(h, s)$  projection if the corresponding points on the  $(h, x)$  plane are known.

Now in a rectifying column the equivalent currents undergo irreversible changes, as described in Chapter IV. Every time the current passes through a plate and when it enters or leaves the evaporator, a transfer of matter and heat occurs within the current between the liquid and the vapour, in that the two phases are brought to or close to equilibrium with each other. Since these processes are irreversible, they entail an increase of entropy  $\Delta S_{\text{irr}}$ . After what we have said in Chapter IV, there will be no difficulty in evaluating  $\Delta S_{\text{irr}}$  and the corresponding  $W_{\text{irr}}$  for the evaporator and for each plate.

In Fig. 96 the  $(h, x)$  diagram of Fig. 94 is shown in conjunction with the corresponding  $(h, s)$  diagram. The points  $L, A, D, G_n, L_n$ , etc., on the latter may be determined graphically from the corresponding

points on the former since they are situated on the boundary curves and have the same values of  $h$ . Whereas the projections of the straight lines  $DL, G_2L_2, \dots$  on the  $(h, x)$  diagram all intersect in  $Z$ , the corresponding lines in the  $(h, s)$  projection will not intersect in a single point,

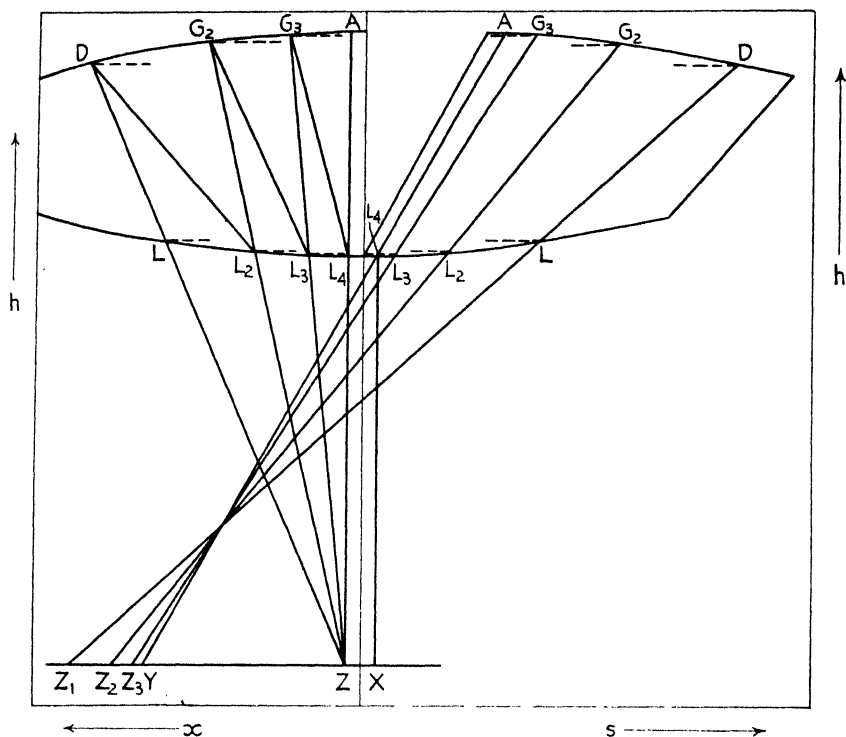


FIG. 96. Schematic  $(h, x, s)$  diagram of air. Determination of irreversible entropy increments

but will intersect the horizontal line  $h = h_Z$  at different points  $Z_1, Z_2, \dots$ . Since the process occurring on a plate is adiabatic (except for heat leaks, which may here be neglected),  $\Delta S = \Delta S_{\text{irr}}$ . Therefore the distance between two adjacent points  $Z_n$  and  $Z_{n-1}$  gives the irreversible change of entropy  $\Delta s_{\text{irr}}$ , incurred by unit mass of equivalent current on passing the plate.<sup>†</sup> It should be noted that  $\Delta s_{\text{irr}}$  must always be positive in the direction of actual flow. Thus, if the current is defined as  $L-G$ , as is usually the case, when  $m_L > m_G$ , and if the plates are numbered from the top downwards,  $s_n$  must be greater than  $s_{n-1}$ .

To determine  $\Delta s_{\text{irr}}$  for the evaporator, we must remember that here

<sup>†</sup> From here on, since we shall be referring to distances on the  $(h, s)$  diagram, i.e. to specific quantities, we shall use small letters.

the process is not adiabatic, but that an amount of heat  $q$  is transmitted to the liquid from without. This leads to a reversible increase of entropy equal to  $q/T_e$ , where  $T_e$  is the temperature in the evaporator. The total increase of entropy will thus be

$$\Delta s = q/T_e + \Delta s_{\text{irr}},$$

so that

$$\Delta s_{\text{irr}} = \Delta s - q/T_e.$$

Now consider the straight line on the  $(h, s)$  diagram corresponding on the  $(h, x)$  side to the line  $AZ$ . Suppose this line to intersect the liquid branch on the  $(h, s)$  side in  $L_4$  and the line  $h = h_Z$  in  $Y$ , and let the line  $s = s_{L_4}$  intersect  $h = h_Z$  in  $X$ . The entropy of the equivalent down-current which enters the evaporator from the last (third) plate will be  $s_Z$ . Then  $\Delta s = Z_3 X$  and, since  $(\partial h / \partial s)_p = T$  and  $L_4 X = q$ ,

$$\Delta s_{\text{rev}} = q/T_e = XY.$$

Therefore

$$\Delta s_{\text{irr}} = Z_3 Y.$$

We have thus determined not merely the total irreversible increase of entropy in the column, which is the length of  $Z_1 Y$ , but, marked off along this line, we have obtained the increase of entropy due to irreversible processes occurring on each plate separately and in the evaporator. So we can tell how much additional work  $w_{\text{irr}} = T_0 \Delta s_{\text{irr}}$  is occasioned by irreversible changes occurring at each point of the column.

**EXAMPLE.** If we return to the example discussed on p. 139, we can now add considerably to the information there given. Firstly, we can determine the number of plates needed to separate the air into 98 per cent. oxygen and 91 per cent. nitrogen, by using the construction shown in Fig. 95. This leads us to the following Table 19, which shows that six plates are theoretically more than sufficient to produce the effect desired, while five plates are too few. In practice rather more plates will be necessary, for reasons that will be discussed in Chapter VIII.

TABLE 19. *Composition of Liquid and Vapour on the Plates of a Simple Column producing 98 per cent. O<sub>2</sub> and 91 per cent. N<sub>2</sub>*

No. of plate	% N <sub>2</sub> in vapour	% N <sub>2</sub> in liquid
1	$D = 91$	$L = 79$
2	84	72
3	68	58
4	39	33
5	16	14
6	5	4
Sump	$A = 1.5$	1.5

The last two values refer to the liquid entering and the vapour leaving the evaporator. Since no liquid oxygen is drawn off and thus all the liquid entering the evaporator leaves it as vapour, no change of composition can occur at this point. The liquid in the evaporator at any given moment, which is being continually replenished while evaporating, will contain as much as 99.7 per cent.  $O_2$  or 0.3 per cent.  $N_2$ .

The work needed to separate the oxygen and nitrogen is the work of compressing the air to 33 atm. The thermal equivalent of this is 2.395 kcal./mole, which amounts to 9.91 kWh. for the 3,000 cub. ft. Since the column is to deal with 3,000 cub. ft. per hour, the power required is 9.91 kW., assuming isothermal compression. In practice, as was shown in Chapter V, this must be multiplied by a factor of about 1.7, owing to frictional losses in the compressor and imperfect cooling. This brings us to a figure of about 17 kW.

The work of separation in the above example corresponds to almost exactly 0.1 kWh./kg. of air, if we neglect the frictional and other losses in the compressor. The reversible work of separation is only about one-tenth of this figure. Most of the work is required to compensate for heat losses (i.e. as refrigeration) and at the same time to make up for irreversible changes in the column. The latter may be computed with the help of the construction shown in Fig. 96. We find that the total increase in entropy, due to the irreversible increments occurring on each plate and in the evaporator, but neglecting that occurring in the throttle valve,† amounts to about 9 cal./mole deg. K. The thermal equivalent of the work  $T_0 \Delta s$ , required to compensate for this, is 2,610 cal./mole of equivalent current  $Z$ . As  $Z = L - D$ ,

$$m_Z = m_L - m_D = 3,000 - 2,600 = 400 \text{ cub. ft.,}$$

or 2/15 of  $m_L$ . The thermal equivalent of this irreversible work is thus 1.040 kcal./mole of air, or just under half the work required to effect the separation.

## 2. The double column

The simple rectifying column has two essential disadvantages. The first is that it can produce pure oxygen only. The nitrogen, as we have seen, is always more or less impure. In the early days of air separation, when nitrogen was of no commercial value, this might hardly have been felt as a drawback. The second disadvantage must have appeared far more serious: large quantities of precious oxygen were wasted.

† This is small as the expanded liquid is supercooled.

Consider a column producing oxygen of practically 100 per cent. purity and the purest nitrogen obtainable, viz. 93 per cent. Let  $L$  be the mixture entering the column and  $A$  and  $D$  the oxygen and nitrogen products respectively, and suppose 1 cub. ft. to enter the plant in a given time. Then

$$m_A + m_D = 1, \quad 0.07m_A + 0.93m_D = 0.79.$$

It follows that  $m_D = 0.83$ ,  $m_A = 0.17$ .

The actual amount of oxygen passing through the column is

$$m_0 = 0.21.$$

Thus  $4/21 = 19$  per cent. of this oxygen passes out with the nitrogen and is lost. The production of 1 cub. ft. of oxygen therefore consumes more energy than it would if all the oxygen contained in the air were extracted from it.

From the general concepts developed in the preceding chapters we may infer that a liquid and a vapour conducted over plates in counter-current can in principle be made to separate into pure components, and if our column is unable to accomplish this, the reason is that it is only half a column. The liquid introduced at the top is indeed rectified as it falls from plate to plate, but the vapour rising from the first plate is simply ejected without further treatment. In order to complete the process, this vapour should be led over more plates and there meet a liquid richer in nitrogen.

A complete column should therefore be a symmetrical piece of apparatus, as shown schematically in Fig. 97 (see also Fig. 62, Chapter III, p. 75). The air would enter in the middle of the column, or rather at a point corresponding to its composition. The evaporator below, in which a quantity of heat  $Q_1$  is transmitted to the liquid, should have its counterpart in a condenser at the top, from which a quantity of heat  $Q_2$  is withdrawn. While liquid oxygen is evaporated below, gaseous nitrogen should be condensed above. An apparatus of this type should produce both components in the pure state.

In distilling oil and alcohol this type of column is actually employed. We must now show why it is inapplicable to air separation. In stills functioning at temperatures above that of the environment, heat is introduced with the help of hot gases heated in a furnace and is with-

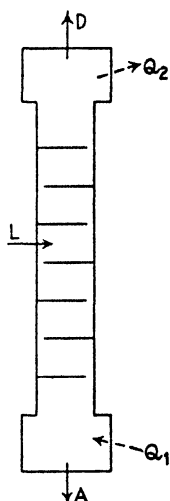


FIG. 97. Development of the double column. First step



drawn by means of water or some refrigerant having room-temperature. The quantities of heat introduced and withdrawn are completely independent of one another, and the temperatures required, being above room-temperature, can always be maintained without the expenditure of mechanical energy. But the separation of air is carried out below room-temperature and the low temperatures must be maintained with the help of refrigerating machinery. Though when the products are finally obtained at room-temperature the sum total of refrigeration vanishes, except for what is needed to compensate for losses, we still require a device to enable us to transfer quantities of heat at certain specified low temperatures. Moreover, in air separation the only refrigerating agent at our disposal is air itself and its products oxygen and nitrogen. If heat is to be withdrawn at a definite temperature, this can be effected only if air, oxygen, or nitrogen can be brought into and maintained in such a state in which they can absorb heat at this temperature. But even if this is possible, the amount of refrigerant available is limited and given by the amount of air passing through the apparatus, unless auxiliary refrigerating cycles are employed, in which the air is not separated but merely absorbs heat.

Now in a column of the kind shown in Fig. 97 the gaseous nitrogen must be condensed at its boiling-point, and this will be the coldest part of the column. Moreover, the temperature of the refrigerating agent must be somewhat lower than that of the substance which is being condensed. In other words, a temperature head must be maintained in the condenser.

What refrigerant is available at a temperature below the boiling-point of nitrogen? We might think of using liquid nitrogen itself, boiling at reduced pressure. But liquid nitrogen is not available; for the nitrogen reaches the condenser as a vapour and we should first have to condense it. The latent heat of evaporation of the nitrogen thus liquefied would therefore have to be employed to condense this same nitrogen, and we cannot use it again to maintain a reflux in the column.

The only refrigerant at our disposal is the liquid oxygen formed in the evaporator, which could be transferred to the condenser, as shown in Fig. 98. In order to make use of it, we must arrange for the column to produce *liquid* oxygen, apart from the vapour emitted from the evaporator to rectify the liquid air. But the temperature of liquid oxygen ( $90^{\circ}\text{K.}$ ) is  $13^{\circ}$  higher than that of boiling nitrogen, that is to say, about  $16^{\circ}$  higher than the temperature needed to liquefy nitrogen

in the condenser. To bring the temperature of liquid oxygen down to  $74^{\circ}\text{K}$ . we should have to lower its vapour pressure to about 9 cm. of mercury. This is quite impracticable in a large-scale technical plant. It is far easier to raise the temperature of boiling nitrogen by increasing the pressure in the column. At 5 atm. abs. the boiling-point of nitrogen

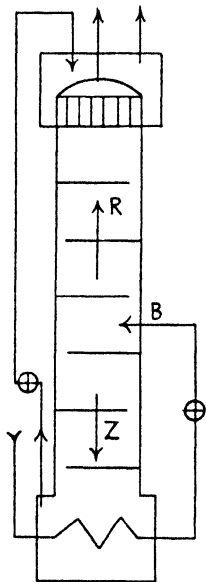


Fig. 98. Development of the double column. Second step

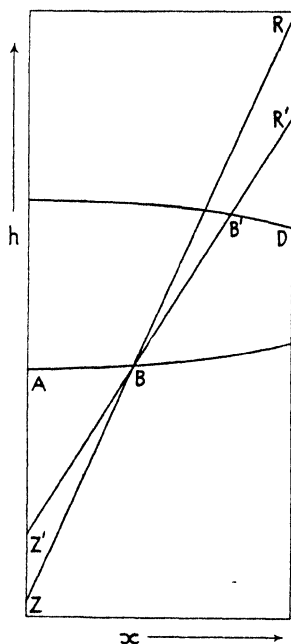


Fig. 99. Limiting line for double column

is about  $94^{\circ}\text{K}$ ., which is well above the boiling-point of oxygen at atmospheric pressure.

Accordingly, the next step towards an apparatus that will yield pure oxygen and pure nitrogen simultaneously is to raise the pressure in the column to about 5 atm. abs.

But this is only one step; for we can show that a column of the type shown in Fig. 98 cannot yield both products in a pure state.

Suppose that Fig. 99 represents the  $(h, x)$  diagram of oxygen-nitrogen mixtures at 5 atm. pressure. The air is admitted to the column of Fig. 98 at  $B$ , either as a liquid or as a vapour or, in the general case, as a mixture of liquid and vapour. In Fig. 99  $B$  is plotted on the liquid branch. Gaseous nitrogen is removed at the top of the column at  $D$  and liquid oxygen at  $A$ . There will then be an equivalent up-current  $R = G - L$  in the upper part of the column and an equivalent down-

current  $Z = L' - G'$  in the lower part. The balance of a section of the column including the inlet  $B$  will thus read

$$B = Z + R.$$

The points  $Z$  and  $R$  on Fig. 99 will thus lie on a straight line through  $B$ . But at the top of the column we have

$$R = D - Q_2,$$

where  $-Q_2$  is the amount of heat withdrawn in the condenser, and at the bottom of the column

$$Z = A - Q_1,$$

where  $Q_1$  is the heat introduced into the evaporator. Therefore

$$x_R = x_D \quad \text{and} \quad x_Z = x_A.$$

So  $R$  is on the line  $x = x_D$  and  $Z$  on the corresponding line  $x = x_A$ , where  $x_D$  and  $x_A$  are the specified compositions of the 'pure' products.

Now let  $BB'$  be the connodal through  $B$ . In order that rectification may proceed,  $RBZ$  must be steeper than  $BB'$ . This can be proved in exactly the same way as we proved the corresponding rule in the case of the simple column. If  $BB'$  and  $RZ$  lie on one straight line, rectification will require an infinite number of plates. The construction for determining the required number will not take us across the diagram. So the line  $Z'BB'R'$  is the line of limiting slope. But  $R'D = Q_2/m_D$  and  $Z'A = Q_1/m_A$  give the minimum amounts of heat required to be withdrawn from the condenser and introduced into the evaporator respectively per unit mass of  $D$  and  $A$ .

Now suppose that we wish to obtain very pure oxygen from our column and at the same time very pure nitrogen; for the purpose of this argument we may put  $x_D = 100$  per cent.  $N_2$ ,  $x_A = 0$  per cent.  $N_2$ . We shall assume the separation to be effected at 5 atm. pressure and the mixture to be introduced at  $B$  as a boiling liquid, which is in fact the most advantageous condition. Then  $B$  will lie on the liquid boundary curve at  $x_B = 79$  per cent. The connodal through this point, on being produced behind  $B'$ , intersects the ordinate axis  $x = 100$  per cent. at  $R'$ , and, referring to the accurate  $(h, x)$  diagram for 5 atm., we find

$$h_{R'} = 2,580 \text{ cal./mole.}$$

Similarly, we obtain

$$h_D = 1,707 \text{ cal./mole.}$$

Therefore

$$R'D = Q_2/m_D = 873 \text{ cal./mole.}$$

This is the amount of heat which must be withdrawn from the condenser for every mole of nitrogen passing out of the column. Now if

both the products are pure, every mole of air entering the column must produce 0.79 mole of nitrogen at  $D$ . So for every mole of air to be separated we must withdraw

$$Q_2 = 0.79 \times 873 = 690 \text{ cal.}$$

from the condenser. All that we have at our disposal to absorb these 690 cal. is the pure liquid oxygen removed at  $A$  and expanded to atmospheric pressure in a valve without change of enthalpy. The latent heat of evaporation of 1 mole of oxygen at 1 atm. pressure is  $\lambda_{O_2} = 1,632$  cal., and for every mole of air we have 0.21 mole of oxygen. Accordingly, we have at our disposal a refrigerating capacity

$$Q'_2 = 0.21 \times 1,632 = 343 \text{ cal.,}$$

which is only half as great as that needed.

This proves that pure oxygen and pure nitrogen cannot be obtained simultaneously in a column of this type.

If we keep to our demand for pure nitrogen, we can see what kind of oxygen this column will give us. Let  $x_A = 40$  per cent.  $N_2$ . We then have

$$m_A + m_D = 1, \quad 40m_A + 100m_D = 79.$$

It follows that  $m_D = 0.65$ ,  $m_A = 0.35$ .

Then the amount of refrigeration needed is

$$Q_2 = 0.65 \times 873 = 568 \text{ cal.,}$$

and the amount of refrigeration available is

$$Q'_2 = 0.35 \times 1,632 = 571 \text{ cal.,}$$

so that  $Q'_2$  just covers  $Q_2$ .

If we wish to obtain pure nitrogen with a single column having a condenser and working at 5 atm. pressure, the richest oxygen product obtainable will contain no more than 60 per cent.  $O_2$ . In fact it will contain less as the column has a finite number of plates and because not the whole of  $\lambda_{O_2}$  is available. Part of the liquid oxygen evaporates on passing through the valve.

In order to obtain pure oxygen and nitrogen simultaneously the impure oxygen product emerging at  $A$  will have to be further purified before it is introduced into the condenser. *This can be done by introducing a set of plates between the inlet  $A'$  and the condenser*, so as to rectify the liquid mixture. This brings us another step forward to Fig. 100, in which pure oxygen may be withdrawn from the condenser-evaporator at  $C$  and pure nitrogen at  $D$ . But this, too, is only a partial solution; for though we may indeed obtain pure oxygen and pure

nitrogen at the same time, we shall still lose the vapour emerging at *E*, which will contain at least as much oxygen as is in equilibrium with the liquid delivered at *A'*. In fact, we seem to have moved in a vicious circle and to have come back to the same point which determined the

inadequacy of the simple column. For we must now again find a refrigerant that will furnish us with liquid nitrogen to rectify this vapour.

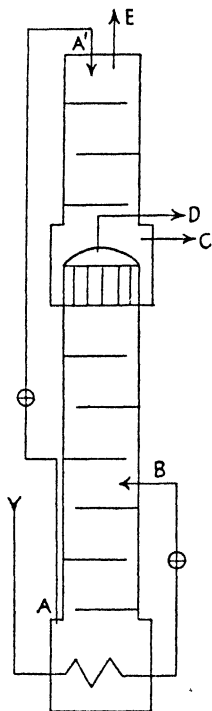
However, this difficulty can be overcome fairly easily. We have seen that liquid nitrogen cannot be made to reproduce itself *and* simultaneously to maintain a reflux in the column. But now the reflux is maintained by the oxygen product and all we require of the nitrogen is self-reproduction. *If we prolong the upper column (Fig. 100) above A' and withdraw liquid nitrogen at D, we can deliver this liquid nitrogen at the summit of the apparatus, allow it to rectify the vapour rising at E which is thereby gradually transformed into oxygen, and finally evaporate it again in the condenser, thus renewing the liquid at D.*

This brings us at length to the complete double column, as shown in Fig. 101, which was evolved by Linde in 1910 and which still predominates in air separation. It appears now as a logical development from first principles, and its prevalence throughout thirty years of technical evolution indicates that the solution was indeed satisfactory.

Fig. 100. Development of double column.  
Third step

The final cycle may be summed up as follows: Compressed air, precooled in a heat-exchanger, enters the evaporator coil at *P*, is expanded to 5 atm. pressure in the valve *V*, and delivered to the middle of the lower column at *B*. Here it is separated into pure liquid nitrogen and a liquid containing about 45 per cent. of oxygen. The latter is withdrawn from the lower column at *A*, expanded to atmospheric pressure in the valve *V*<sub>O</sub>, and admitted in the middle of the upper column at *A'*. The liquid nitrogen collects in the trough below the condenser, whence it is removed at *E*, expanded to atmospheric pressure in the valve *V*<sub>N</sub>, and admitted at the top of the upper column at *E'*. Finally, gaseous oxygen is withdrawn immediately above the condenser at *C* and gaseous nitrogen at *D*.

The process is represented graphically in Fig. 102, in which the (*h*, *x*)



curves for 5 atm. and 1 atm. are superposed. If we assume the air at  $B$  to be a saturated liquid,  $B$  lies on the liquid curve for 5 atm. at  $x_B = 79$  per cent.  $N_2$ . At  $B$  the air separates into an equivalent down-current  $Z$  and an equivalent up-current  $R$ , so that  $B = Z + R$ . Moreover,  $Z = A - Q_1$  and  $R = E - Q_2$ , where  $-Q_2$  is withdrawn from the condenser and  $Q_1$  supplied to the evaporator. So  $Z$  lies directly below  $A$  and  $R$  directly above  $E$ . The composition of  $A$  can be chosen arbitrarily within certain limits. We have seen that  $x_A$  must be greater than 40 per cent.  $N_2$ , and we shall see presently that a still more stringent condition exists. We shall assume that  $x_A$  has been fixed at 55 per cent.  $N_2$ .

The 'rich air' withdrawn at  $A$ , after expansion to  $A'$ , again separates into two equivalent currents  $R'$  and  $Z'$ , so that these two points lie on a straight line through  $A'$ , which coincides with  $A$ , as expansion in a valve does not alter the enthalpy. The same argument as that used with reference to the lower column shows that  $R'$  must lie directly above  $D$  and  $Z'$  below  $C$ . The actual position of the four points  $Z, R, Z', R'$  has yet to be determined.

This may be done with the help of six balance equations, derived from the various parts of the apparatus, some of which we have already mentioned and all of which may be deduced directly from Fig. 101.

$$\begin{aligned} R' &= D - E', & A' &= R' + Z', & Z' &= C + Q_2, \\ R &= E - Q_2, & B &= R + Z, & Z &= A - Q_1. \end{aligned}$$

The unknowns in this series of equations are  $Z, Z', R, R', Q_1, Q_2$ . Of the other terms we know

the  $x$ - and  $h$ -values but, except for  $B$ , we do not know the  $m$ 's. But these may be determined from the  $x$ -values alone with the help of  $m_B$ . Thus

$$m_D + m_C = m_B, \quad m_D x_D + m_C x_C = m_B x_B \quad \text{determine } m_C \text{ and } m_D;$$

$$m_A + m_E = m_B, \quad m_A x_A + m_E x_E = m_B x_B \quad \text{determine } m_A \text{ and } m_E.$$

After this we can find the unknowns from the six equations separately in the order in which they are written.

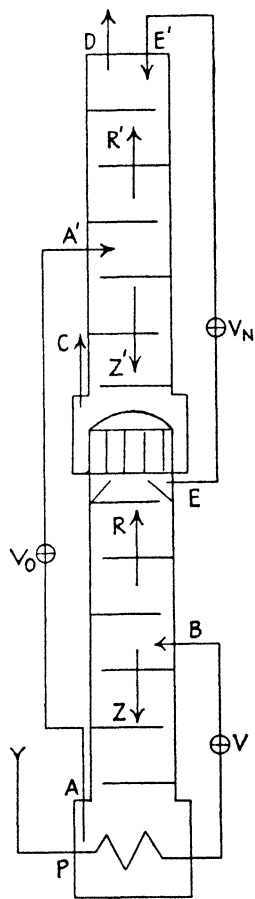


FIG. 101. Linde double air column

We see that the arbitrary determination of  $x_A$  actually fixes all the other points of the column, including points  $R'$  and  $Z'$ . But in the upper column, as well as in the lower, we have a condition for  $x_A$ . For

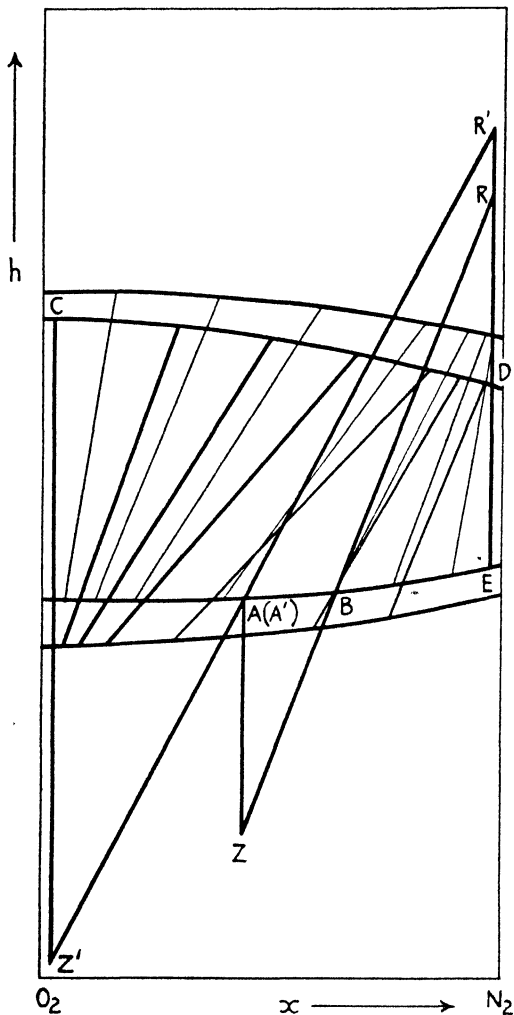


FIG. 102. Representation of double air column on  $(h, x)$  diagram

$R'Z'$  must be steeper than the connodal through  $A'$ . In practice this brings  $x_A$  considerably higher than 40 per cent.  $N_2$ .

Since in the double column the liquid mixture that collects in the lower evaporator contains only 45 per cent. of oxygen, very little is required of the bottom half of the lower column. A liquid in equilibrium

with atmospheric air will, in fact, contain almost this percentage of oxygen without further rectification. It thus appears natural to go one step farther and discard the bottom half of the lower column altogether. The air can then be introduced as a saturated vapour at the bottom of the column, and the liquid that will collect in the sump will contain about 40 per cent. of oxygen. Some commercial plants are designed in this way.

The idea of introducing the air in the vapour state at the bottom of the plant led Claude to discard the entire lower column and to replace it by a dephlegmator. From what has been said in Chapter III it is evident that this solution is perfectly feasible. We shall treat it in greater detail in the next chapter.

If we determine and analyse the work needed to bring about a complete separation of oxygen and nitrogen in the double column, we find that, as in the simpler plant outlined in the last section, the power consumption is very much greater than the reversible work of separation. Some figures will be given later when we come to discuss commercial plants. As before, a considerable part of this work is due to the irreversible processes on the plates and in the evaporator and condenser. If  $\Delta S$  is the sum of all irreversible entropy increments occurring in the plant, an amount of work equal to  $T_0 \Delta S$  will have to be expended, over and above  $W_{\text{rev}}$ . When the products of separation are obtained as gases at room-temperature, the only way to perform this work is to compress the gas to a higher pressure than would be necessary if  $W$  were equal to  $W_{\text{rev}}$ .

Now in the case of air, compression is not merely an expenditure of work, but also a source of refrigeration. Since  $(\partial H / \partial p)_T < 0$ , isothermal compression leads to a decrease in enthalpy. This is, in fact, the only source of refrigeration in the Linde air liquefiers, as was shown in Chapter V. If, as is theoretically the case, no refrigeration were needed in the stationary state to separate oxygen and nitrogen, we should have to get rid of the refrigeration by heating the gases artificially at some point of the apparatus; for we cannot perform work on air without eventually cooling it. Actually, as was mentioned in Chapter IV, the separation of gases does require refrigeration, owing to heat leakage from the surroundings. Where the object is to obtain liquefied gases, and the required refrigerating performance, and therefore the power consumption, is relatively high, the heat leakage plays a subordinate role. But where gaseous products are being obtained, the power consumption is very much smaller; the reversible work of separation is



much less than the reversible work of liquefaction. In this case, the heat leakage is not merely the only cause necessitating refrigeration, it is also one of the most important causes of additional power consumption. In fact we need not only refrain from heating our gases to get rid of the refrigeration due to compression and expansion, but we must, on the contrary, compress our gases still more to increase the refrigerating performance.

The refrigerating performance necessary to make up for losses through the lagging and for imperfect heat transfer in the exchangers and accumulators is the decisive factor in the designing of separating plant. It was for this reason that we discussed in detail in Chapter V the various methods of refrigeration and liquefaction.

## VII

### THE SEPARATION OF AIR (2)

#### COMMERCIAL AIR SEPARATION

1. ALL the methods of air liquefaction described in Chapter V have been applied in conjunction with the devices discussed in Chapters III and VI to the problem of separating air into its components, this being indeed the object for which they were invented. We saw that three main types of liquefier have been developed:

- (i) The Linde plant, with high-pressure cycle and ammonia refrigerator.
- (ii) The Claude plant, with an expansion cylinder working entirely at low temperatures, and a working pressure of 40 atm.
- (iii) The Heylandt plant, with an expansion cylinder which the air enters at room-temperature and at 200 atm.

We saw that the efficiency of the first two types was virtually the same, and that of the Heylandt plant was somewhat higher. The quadruple cascade, which should in theory be the most efficient of all, has not yet asserted itself in commercial practice.

In air liquefaction, where the only object is to liquefy air as cheaply as possible, it is simple to determine which is the most efficient apparatus, but in air separation this will depend on the object we have in view.

Historically, the first object in air separation was to produce cheap gaseous oxygen, and to this day this is the most important field of application. Large quantities of oxygen are employed for oxy-acetylene welding and numerous other purposes, and this oxygen is usually compressed into steel cylinders and stored and transported therein. As time went on, the demand for oxygen continued to increase, and, at the same time, the demand for higher purity.

Subsequently, as the weight and bulk of steel cylinders became more and more irksome, oxygen began to be handled in the liquid state. With the development of efficiently lagged transport and storage tanks and of small-scale metal vacuum vessels, it became more and more economical for the manufacturers to distribute and for the consumers to purchase liquid oxygen and to let it evaporate naturally or artificially at the place of its application. At present the demand for liquid oxygen is growing more rapidly than that for gaseous oxygen, though the consumption of gas still preponderates in most countries.

With the development of the synthetic ammonia industry, which set in shortly after 1920, a demand for nitrogen arose, which has been growing rapidly ever since. This introduced quite a new outlook in air separation. Up to that time nitrogen had been a waste product, and a very irksome waste product indeed, since it comprised four-fifths of the air separated. Moreover, the only urge for producing pure nitrogen had been the desire not to waste oxygen. But the nitrogen required for synthesizing ammonia must be very pure indeed, as even small admixtures of oxygen have a detrimental effect on the catalysts. Thus it became important to produce pure oxygen and pure nitrogen simultaneously, which set an increasingly high standard for the design of separating plant.

In the ammonia industry, the air-separating plant and the synthesizing plant are usually situated in one building. The nitrogen need not therefore be transported in cylinders, but can be fed from its source to the synthesizer in a short pipe-line. There is thus no point in producing the nitrogen as a liquid, which would merely entail an unnecessarily high power consumption. Liquid nitrogen is in demand only in the laboratory for the liquefaction of hydrogen and helium in small quantities and as a cold reservoir for physical experiments at low temperatures. Its role in separating coke-oven gas will be described in detail in Chapter X.

From these remarks we may draw the conclusion that the efficiency of a liquefier will determine that of a separating plant only when liquid oxygen is to be obtained, i.e. when the refrigerating performance required in the separator is of the same order of magnitude as in the case of a liquefier. When both the products are to be gained in the gaseous state, and the refrigerating performance consists only in compensating for heat leakage, other considerations will predominate. Thus we find that the Heylandt separating plant is not the most useful apparatus for producing gaseous oxygen.

The various plants described in detail are numbered consecutively through the chapter.

## **2. Linde air-separating plants**

The Linde Company manufacture four main types of air-separating plants, which are designed to produce gaseous oxygen and, in some cases, gaseous nitrogen. All four are perfectly logical combinations of a Linde air liquefier with the rectifying columns described above.

*No. 1.* The most primitive type combines a simple liquefier with

a single column and, naturally enough, furnishes oxygen only. The air is compressed in four stages. Between the second and third stages carbon dioxide is removed by passing the air through a solution of caustic potash. After the fourth stage the air traverses an oil trap and several cylinders filled with solid caustic soda to absorb the moisture. Thereupon it passes through a heat-exchanger and thence through the coil in the evaporator of the column. Finally, it is expanded to atmospheric pressure and delivered, almost completely liquefied, at the top of the column, as shown in Fig. 93. Gaseous oxygen is withdrawn from the top of the evaporator and impure nitrogen from the summit of the column. Both products return through the heat-exchanger. The oxygen is collected in a gas-holder and subsequently compressed into cylinders. The nitrogen is discarded.

Before the stationary state is reached, the working pressure is kept at 200 atm. In the stationary state, from 50 to 65 atm. are needed to cover the heat leaks,<sup>†</sup> which depend on the size of the plant. This type of separator is evidently uneconomical, as only about 65 per cent. of the oxygen in the air is obtained as a product, the rest escaping with the nitrogen. Its only advantage is its simplicity, and it is manufactured on a small scale only, for laboratory purposes or for small factories requiring oxygen and situated far from the distributing centres. The largest plants of this type are designed for 1,400 cub. ft. of oxygen per hour.

No. 2. The second type of Linde air separator, which is built to produce up to 2,800 cub. ft. of oxygen per hour, differs from the first only in that a double column is used instead of a simple still. Compression and purification are carried out as before; whereupon the air is expanded to 5 atm. after passing through the heat-exchanger, and introduced in the middle of the lower column, as shown in Fig. 101. The double column itself has already been described on p. 152. In the stationary state the working pressure is between 40 and 60 atm.

This apparatus is much more efficient than the first and enables nitrogen as well as oxygen to be obtained. However, it is usually difficult to produce both simultaneously in a state of high purity. This is due partly to the difficulty of maintaining steady conditions in the column over long periods, and partly to the presence of 0.94 per cent. argon in the air (see Chapter IX), which impedes rectification and must finally appear in one of the products. The following table gives the oxygen content of simultaneous products, as obtained in practice in

<sup>†</sup> Rather more than in the example discussed in Chapter VI.

the double column. The argon may, to a certain extent, be distributed at will.

TABLE 20. *Oxygen Content in Products of Linde Double Column*

<i>Per cent. oxygen in products.</i>	
<i>Oxygen product</i>	<i>Nitrogen product</i>
95	0.1
97	0.2
98	0.3
98.5	0.4
99	1.0
99.5	2.0
99.7	4.0

No. 3. We have seen that 40–60 atm. are needed in the apparatus last described to maintain the stationary state. This, as we know from Chapter V, is due to the low refrigerating performance achieved by compression at room-temperature. It is natural that Linde should have applied the auxiliary ammonia cycle to raise the efficiency of the separating plant. In the arrangement shown in Fig. 103 the ammonia cycle simultaneously serves to freeze out water vapour, so that no caustic soda is needed. This further reduces the costs of oxygen and nitrogen.

The Linde double column with ammonia cycle is typical of large-scale air-separating plant and may therefore be described in somewhat greater detail. In the potash tower *T*, in which carbon dioxide is removed after the second stage of compression, a current of caustic potash solution is kept circulating with the help of a pump *P*. The air is then further compressed and thereupon precooled to  $-15^{\circ}\text{C}$ . in one of two heat-exchangers  $E_1$ . The refrigerants in  $E_1$  are oxygen and nitrogen, emerging from the main heat-exchanger *E*.  $E_1$  is simultaneously a trap, in which water vapour is frozen out. The warm air passes through both exchangers in series, while the refrigerant traverses only that section which the air enters last, and in counter-current to the latter. When the passage begins to become blocked, the currents are reversed. The warm air thereupon thaws the ice in the section that was cooled in the last period and is itself cooled in the other section. Nevertheless, a certain amount of water vapour remains in the air, and so the next pair of heat-exchangers  $E_2$ , which are cooled with ammonia, are constructed similarly. While the air is being cooled in section *a* by means of liquid ammonia, boiling at reduced pressure, the layer of ice is removed from section *b* by a current of warm ammonia vapour. When a rising pressure head between the top and bottom of *a* shows that the

ice layer here is becoming thick, the currents are reversed. Usually the ammonia vapour can be turned off before it is time to reverse the current, and then one of the sections simply ceases to function for a time.

After being cooled in  $E_2$  to about  $-45^\circ\text{C}$ ., the compressed air passes through the main exchanger  $E$ , whereupon the cycle is continued as

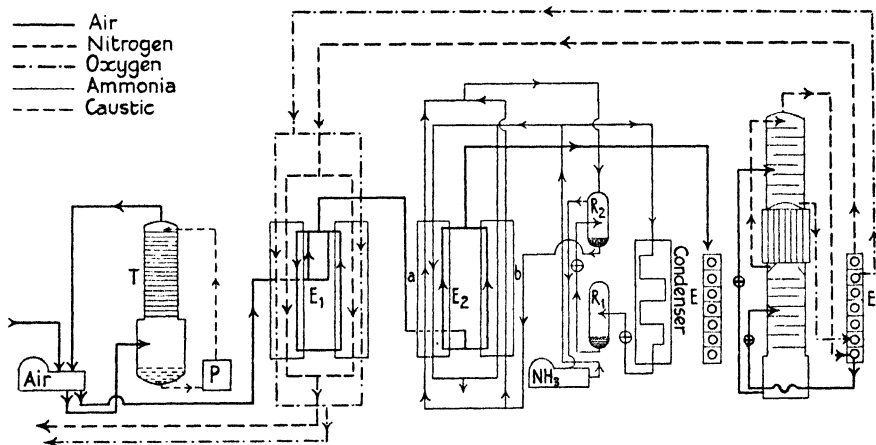


FIG. 103. Linde double air column with ammonia cycle

in (2). The ammonia is made to boil at a pressure of 35 cm. of mercury, thus bringing its temperature down to  $-48^\circ\text{C}$ . This is achieved with a so-called 'compound refrigerator'. The liquid ammonia is first expanded from 10 atm. to about 2 atm., which is the pressure behind the first stage of the ammonia compressor. From the bottom of a reservoir  $R_1$  at this pressure, the ammonia is expanded to a low-pressure reservoir  $R_2$ , from which it passes to the bottom of  $E_2$ . The ammonia vapour from  $E_2$  is delivered to the top of  $R_2$  and thence passes directly to the compressor at low temperature. The air and the ammonia traverse  $E_2$  in the same direction since, owing to the height of the heat-exchanger, the liquid is colder at the top than at the bottom.

This apparatus is more efficient than (2), but rather complicated. It is profitable only for large-scale plant. The working pressure in the stationary state varies from 20 to 30 atm. Whereas the separating plants of type (2) are designed only for a run of from 10 to 12 days, those of type (3) can run for a month on end without warming up.

*No. 4.* In the apparatus hitherto described the refrigeration needed to compensate for heat leakage was achieved by raising the pressure of all the air passing through the plant, with or without an auxiliary

ammonia cycle. We have seen that, in a large plant and with the help of ammonia, this pressure can be reduced to 20–30 atm. It is in keeping with the Linde principle, as discussed in Chapter V with reference to the high-pressure liquefaction cycle, to separate as far as possible the refrigerant as such from the air which is being treated. The air-separating plant with high-pressure cycle is the logical development of this idea. In this apparatus the bulk of the air to be separated, about 75 per cent. of all the air entering the plant, is compressed only to the pressure required in the lower column, i.e. to about 5–6 atm. This air does not pass through the coil in the evaporator, but is introduced as a saturated vapour at the bottom of the lower column. This can be done because saturated air is more or less in equilibrium with the liquid in the evaporator, which contains about 40 per cent. of oxygen. The remaining 25 per cent. of air, the refrigerant proper, is brought to a high pressure and treated as in the apparatus heretofore described. At first this air is maintained at 200 atm.; when the stationary state has been reached, the pressure is reduced to 70–100 atm. The work required to compress 75 per cent. of the air to 5 atm. is roughly equal to the theoretical work of separating oxygen and nitrogen. The compression of 25 per cent. to 100 atm. is merely needed to compensate for the heat leaks and thus represents 'pure' refrigeration.

This device, combined with the ammonia cycle, is the most efficient aggregate of the Linde type. It is also the most complicated and can therefore be applied to advantage only on a large scale. It is used mainly for the production of gaseous nitrogen, intended for ammonia synthesis, as very large oxygen aggregates are seldom needed. As in (3), moisture is frozen out and not removed chemically.

The separate air circuits necessitate rather an intricate system of heat-exchangers, which are shown in the diagrammatical sketch on Fig. 104. We now have two pairs of heat-exchangers  $E_1$  and  $E'_1$  before the ammonia cooler,  $E_1$  for the low-pressure air and  $E'_1$  for the high-pressure air. The former is cooled with nitrogen, the latter with oxygen. Similarly, we have two ammonia heat-exchangers,  $E_2$  and  $E'_2$ . The former, traversed by low-pressure air, is double; the latter, traversed by high-pressure air, is a single exchanger of helical form. The helical heat-exchanger  $E$ , which in (2) and (3) cooled down the entire supply of air to the temperature obtaining in the evaporator, here cools only the high-pressure air with the help of oxygen vapour. The larger low-pressure current traverses two tubular heat-exchangers  $E_3$  and  $E_4$ , which are cooled with nitrogen. By giving  $E_3$  two parallel sections,

the last traces of moisture can be removed and the plant can be made to function for three months without stopping. The ammonia cycle is similar to that described in (3). Apart from the fact that most of the air enters the lower column as a vapour from below, the actual separation process is the same as in the previous types.

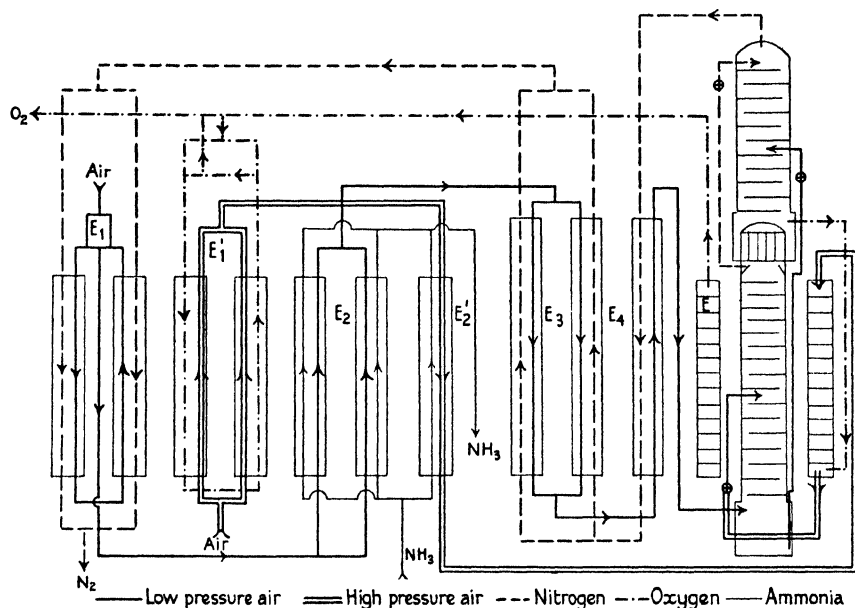


FIG. 104. Linde double air column with high-pressure and ammonia cycles

The Linde double column with low- and high-pressure cycles and ammonia refrigeration is used for very large aggregates. It may therefore be of interest to give some details concerning one of them. Some years ago the Linde Co. built a series of large plants to produce pure nitrogen for the synthetic ammonia industry. The purity of the nitrogen was 99.96 per cent., the oxygen leaving the plant was only 94 per cent. and was not further used. The double column was 31½ ft. high. The lower column contained 24 plates, 3 ft. in diameter; the upper column had 35 plates with a diameter of 3 ft. 5 in. The main condenser-evaporator consisted of 6,973 tubes, each about ¼ in. in diameter and 4 ft. 2 in. long. 230,000 cub. ft. of air were separated per hour; of these 49,400 were compressed to 120 atm., the rest to 5 atm. The plant gave 176,500 cub. ft. of pure nitrogen per hour.

Fig. 105 is a photograph of the condenser-evaporator of a large nitrogen plant. A drawing of a similar condenser-evaporator is shown



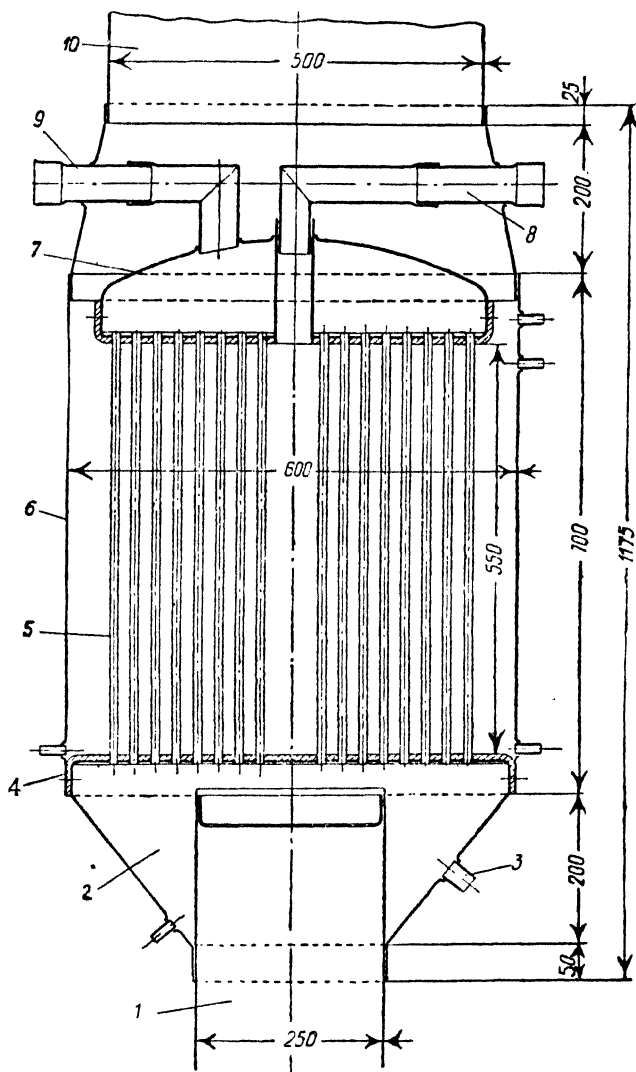


FIG. 106. Condenser-evaporator  
(dimensions in mm.)

- |                               |                                    |
|-------------------------------|------------------------------------|
| 1. Lower (pressure) column    | 6. Casing of condenser-evaporator  |
| 2. Trough for liquid nitrogen | 7. Dome                            |
| 3. Outlet for liquid nitrogen | 8. Outlet tube for gaseous oxygen  |
| 4. Plate for tubes            | 9. Connecting tube to safety valve |
| 5. Tubes of condenser         | 10. Upper column (low pressure)    |

in Fig. 106. In Fig. 107 a large plant is shown in the course of assembly. Part of the main heat-exchanger is visible below and another part is seen coiled around the upper column. Between them is the casing of

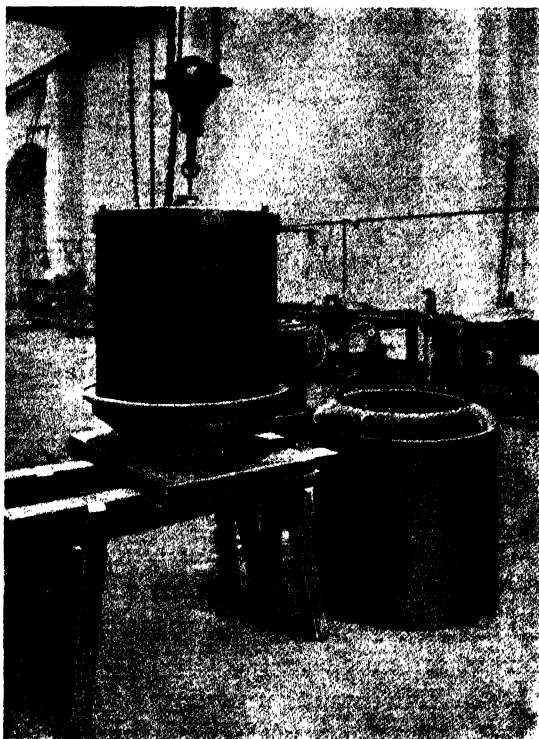


FIG. 105. Condenser-evaporator.  
Height about 2 ft. 6 in.



FIG. 107. Assembly of large separating plant

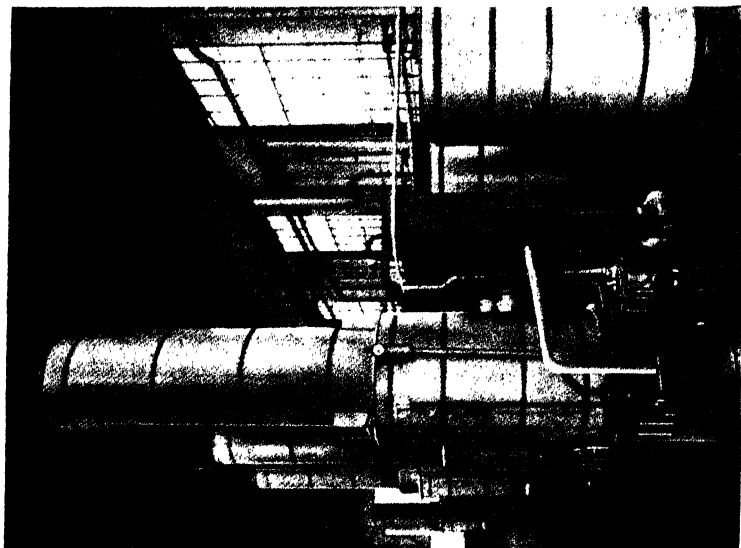


FIG. 108. Plant for producing nitrogen for synthetic ammonia. Height of columns about 16 ft.

the condenser-evaporator. Fig. 108 shows a group of nitrogen units in a German factory.

### 3. Heylandt air-separating plant

No. 5. The Heylandt liquid-oxygen plant is shown in diagram in Fig. 109. The working pressure is 200 atm. The compressed air is con-

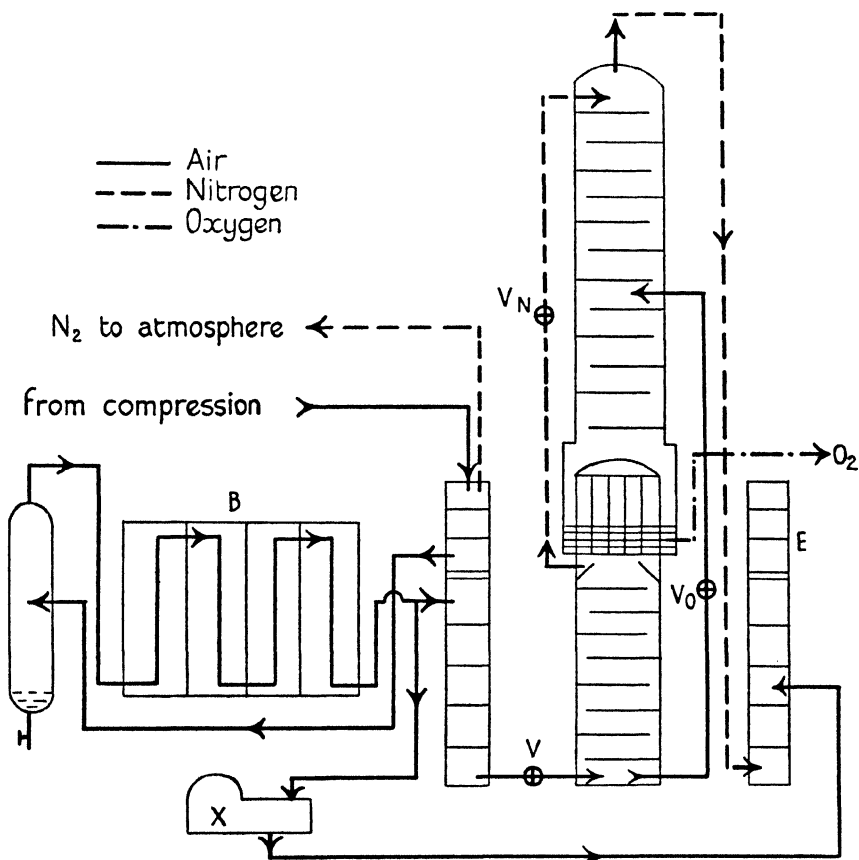


FIG. 109. Heylandt liquid-oxygen plant

veyed directly from the compressor, after purification from carbon dioxide, to the upper section of the heat-exchanger *E*, where part of the moisture is condensed and withdrawn. The compressed air is finally dried in the caustic-soda battery *B*, after which it divides: 40 per cent. is passed straight through the lower section of *E* to the valve *V* and there expanded to about  $4\frac{1}{2}$  atm., in the course of which part of it is liquefied. The remaining 60 per cent. is expanded in the cylinder of

the expansion engine  $X$  to the same pressure, and is thereby cooled to about  $-135^{\circ}\text{C}$ . The expanded cold air re-enters the heat-exchanger at the point where the compressed air is at this temperature, and is cooled further in separate tubes along with the latter. The double column itself is exactly the same as those formerly described, except that there is no coil in the evaporator. All the air, partly liquid and partly vapour, is delivered at the bottom of the lower column. The vapour rises to the summit, while the liquid is transferred through the 'oxygen valve'  $V_0$  to the middle of the upper column, as in the Linde plants. The liquid oxygen is withdrawn from the space between the tubes of the condenser-evaporator. The plant can also be made to supply liquid nitrogen, which is withdrawn from the trough at the top of the lower column. If gaseous oxygen only is required, the expansion engine can be turned off completely and the pressure lowered to about 60 atm.

The main heat-exchanger in the Heylandt plants is often of the Hampson type and is mounted on the top of the column. Coils of narrow high-pressure tubing are wound horizontally in funnel-shaped jackets, through which the low-pressure gases are passed. The exchanger, a drawing of which is given in Fig. 110, consists of two concentric sections, which are cooled with nitrogen and oxygen respectively.

#### 4. 'Air Liquide' air-separating plants

The principal feature of the Linde and Heylandt separating plants is their straightforwardness. The apparatus may be deduced quite logically from first principles; each plant is built up of a few standard elements, and there are no ingenious 'gadgets'. It is when we come to the plants designed by the French firm 'Air Liquide', in which the many inventions of Georges Claude have materialized, that we realize that the simple solutions of Linde are not as unique as they appear at first sight. The four French aggregates, now to be described, present a wealth of interesting detail, totally absent in the German plants. They are very probably no better than the Linde and Heylandt separators, but they are infinitely more imaginative.

Claude's use of the expansion engine is guided mainly by the desire to work it at low pressures and low temperatures, and its position in the plant is dictated by the relative importance of the function it has to fulfil. Moreover, we shall see that, by suitable use of dephlegmators, great variety may be introduced into the separation process itself.

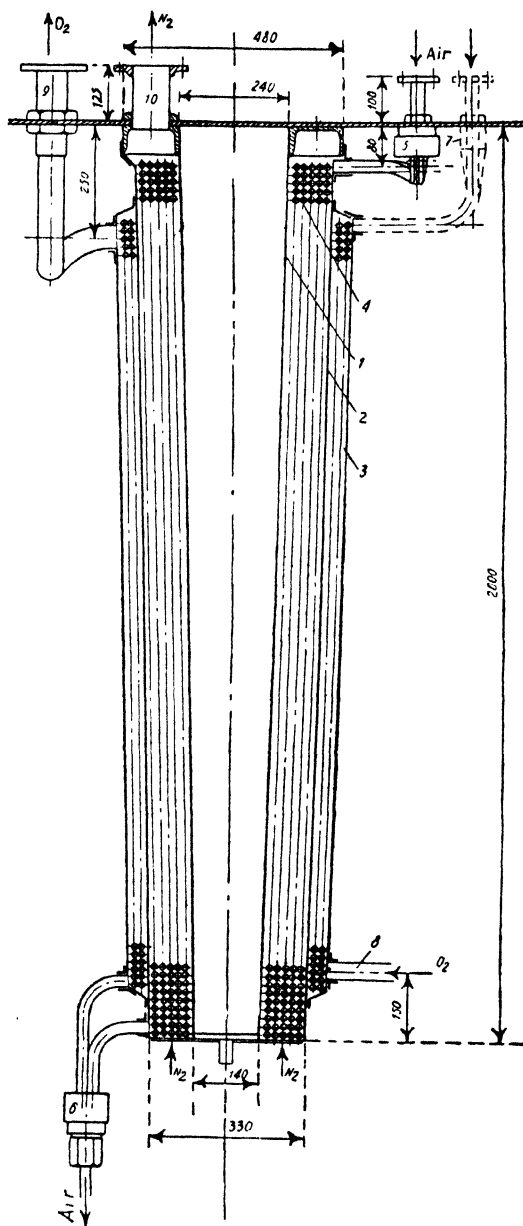


FIG. 110. Heylandt heat-exchanger, Hampson type  
(dimensions in mm.)

- |                         |                              |
|-------------------------|------------------------------|
| 1. Inner jacket         | 6. Air outlet                |
| 2. Intermediate jacket  | 7. Air inlet (outer section) |
| 3. Outer jacket         | 8. Oxygen inlet              |
| 4. High-pressure tubing | 9. Oxygen outlet             |
| 5. Air inlet            | 10. Nitrogen outlet          |

No. 6. The simplest 'Air Liquide' aggregate is the so-called Le Rouget plant for small-scale liquid oxygen manufacture, the characteristic feature of which is an expansion engine on the return line of impure nitrogen (see Fig. 111). Air, compressed to 200 atm. and suitably purified, traverses the two heat-exchangers 1 and 2 in series,

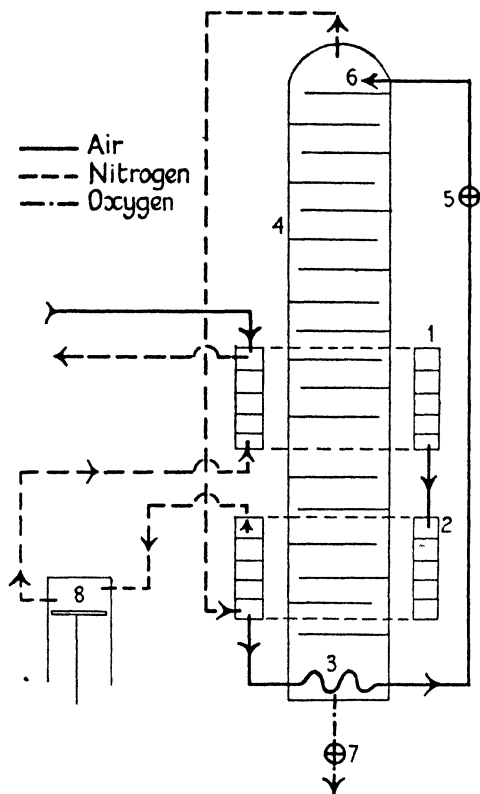


FIG. 111. Le Rouget plant for liquid oxygen

whence it passes through the coil 3 in the single column 4. It is then expanded to 4 atm. in the valve 5 and delivered, mostly in the liquid state, at the top of the column at 6. Pure liquid oxygen is withdrawn through the valve 7. Impure gaseous nitrogen is passed through the heat-exchanger 2, in which it is warmed up to  $-60^{\circ}\text{C}.$ , and is then again cooled in the expansion engine 8, in which its pressure is reduced from 4 to 1 atm. It is then brought up to room-temperature in the heat-exchanger 1 and emitted to the atmosphere.

From previous discussions it is apparent that this apparatus cannot be very efficient. The working pressure is 200 atm. and much oxygen

is wasted. Yet it is comparatively simple and useful for small-scale liquid oxygen production.

*No. 7.* For large-size gaseous nitrogen and oxygen plants Claude now uses a double column similar to the Linde type, except for a few important details, an expansion engine in the high-pressure line, and a peculiar type of heat-exchanger, which appears in all large-scale plants of the 'Air Liquide'. These heat-exchangers consist of wide baffled tubes, in which the incoming gas is cooled and in some cases partially liquefied at the expense of outgoing cold products, the latter passing through narrow vertical tubes within the exchangers.

The first exchanger 1 *a* and 1 *b* (see Fig. 112) is of the double, alternating variety, so that ice may be easily removed; the second, in which the air is partially liquefied, is single. The pressure is 25 atm. at first and about 16 atm. when the stationary state is reached. About one-third of the compressed air passes right through 2 and from there to the coil 3 at the bottom of the lower column, where it is completely liquefied. It is then expanded to 4 atm. in the valve 5 and delivered to the middle of the lower column at 6. Two-thirds of the air is withdrawn from the middle of 2 and passed through the expansion engine 7, in which the air is expanded to 4 atm. and cooled almost to saturation point. It is then admitted as a vapour to the bottom of the lower column. The double column is rather similar to that used in the Linde plants, except for the fact that it has two condenser-evaporators. All the oxygen that evaporates between the tubes of the principal condenser-evaporator 8 is used to carry on the rectifying process in the upper column. The final oxygen product is drawn off from the subsidiary condenser-evaporator 9, which is always situated well below the level of 8 and separated from the rest of the plant by armoured plate. Only part of the nitrogen is liquefied in 8, the rest passing together with the liquid from the trough 10 to the tubes of 9, where it is completely liquefied. The tube 11, which conducts liquid oxygen from 8 to 9, is connected to the lowest point of the former. The object of this arrangement is to allow all impurities in the liquid oxygen, such as dissolved acetylene, that may give rise to explosions, to collect in 9. Should an explosion occur, it can thus be localized in 9 by means of the armoured plate, and the subsidiary condenser-evaporator may be removed easily without taking the rest of the plant to pieces.

The trough 10 differs from those employed in the Linde plants in that it is closed on the inside. Thus the liquid collecting in the trough must have passed right through the centre of 8 as a vapour and



have condensed in the outer tubes afterwards. This device ensures a greater purity of the nitrogen than would otherwise have been obtainable.

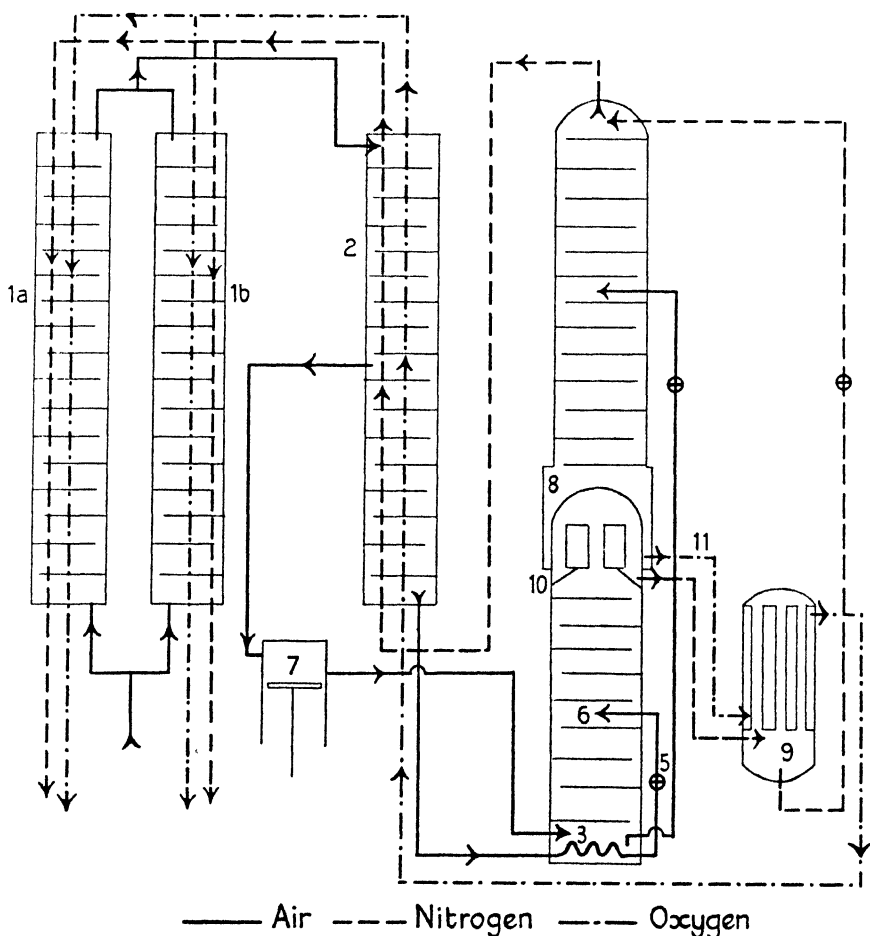


FIG. 112. Claude double air column for gaseous nitrogen and oxygen

Both the final products of the plant are passed through the whole of 2 and of 1a or 1b and collected at room-temperature.

This is the most economical of the Claude aggregates and, at the same time, bears the greatest resemblance to the Linde and Heylandt plants. The smallest model separates 133 cub. m. (4,700 cub. ft.) of air per hour, the largest 2,660 cub. m. (94,000 cub. ft.). The aggregates can produce a nitrogen product of 99.7 per cent. purity or 99 per cent. oxygen. The pressure in the stationary state is 35 atm. for the smallest

type and 15 atm. for the largest. The large plants can run for thirty to forty days without warming up.

No. 8. The remaining two 'Air Liquide' plants which we shall treat here are of the so-called  $1\frac{1}{2}$ -column type. One of these, which produces

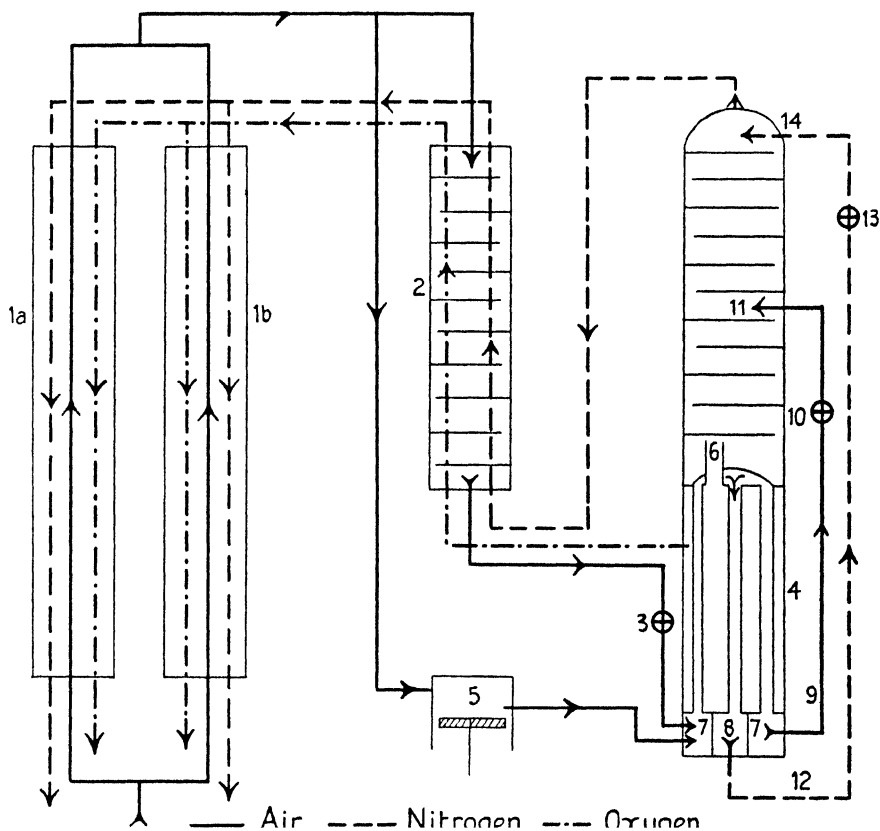


Fig. 113. Claude plant for gaseous oxygen with dephlegmator

gaseous oxygen and nitrogen, seems to have been replaced by type (7) in recent years. Not long ago, however, it was considered the most ingenious and successful aggregate.

After traversing the preliminary heat-exchanger 1a or 1b (Fig. 113), the compressed air divides. One portion is partially liquefied in 2, expanded to about 4 atm. in the valve 3, and admitted to the bottom of the tubes of the dephlegmator 4. The rest is expanded in the engine 5 to the same pressure and admitted, together with the liquid, at the same place. The liquid boiling between the tubes of the dephlegmator is pure oxygen, delivered through a tube 6 from the lowest plate of the

column. The collector below the tubes of the dephlegmator is divided into a central chamber 8 and an external annular space 7 by a cylindrical partition. A mixture composed of liquid introduced from 2 and liquid condensed in the external tubes of the dephlegmator collects in the annular space 7 and is thence withdrawn in the tube 9, expanded to atmospheric pressure in the valve 10, and delivered in the middle of the column at 11. The nitrogen escaping from the top of the external dephlegmator tubes is forced down the central tubes, where it is completely liquefied, collecting in the central chamber 8. Thence it is withdrawn through the tube 12, expanded in the valve 13, and admitted at the top of the column at 14. The two gaseous products are returned through 2 and 1*a* or 1*b*. Through having to pass down the central tubes of the dephlegmator, the liquid nitrogen becomes purer than would otherwise have been possible without having recourse to a second plate column. A further cylindrical partition, not shown in the figure, separates the space between the tubes of the dephlegmator into an outer and an inner chamber, and liquid oxygen is introduced through 6 into the inner portion only. Liquid can pass into the outer chamber only by overflowing across the partition. All the oxygen evaporating from the central chamber returns to the column. Only oxygen from the outer space is removed as the final product. In this way the central tubes of the dephlegmator are kept well covered with liquid to the top, which facilitates the condensation of nitrogen within, and the oxygen product is further purified by distillation in the central chamber. The working pressure of these plants is about 25 atm.

*No. 9.* The large-scale liquid oxygen plant of 'Air Liquide' (Fig. 114) is characterized by a dephlegmator and double expansion engine. After passing through the preliminary heat-exchanger 1*a* or 1*b*, at 60 atm. pressure, part of the air traverses the 'liquefier' 2 from top to bottom and is admitted to the base of the dephlegmator after expansion to 4 atm. The rest is expanded, likewise to 4 atm., in the first stage of the expansion engine 3, after which it again separates into two portions. One is added to the partially liquid air behind the valve; the other is warmed by passing up the upper part of 2, and is then expanded to 1 atm. in the second stage of the engine. The expanded air thereupon mixes with the cold nitrogen vapour emerging from the top of the column, and returns through the lower part of 2 and through 1*a* or 1*b*. The oxygen in this air is wasted.

The dephlegmator has none of the complications described in (8). The refrigerant between the tubes is liquid oxygen from the column,

part of which is withdrawn through the tube 9. The liquid mixture from the sump is expanded to 1 atm. in the valve 6 and admitted in the middle of the column. The nitrogen vapour escaping from the summit of the dephlegmator is liquefied in a coil 7 inside the column

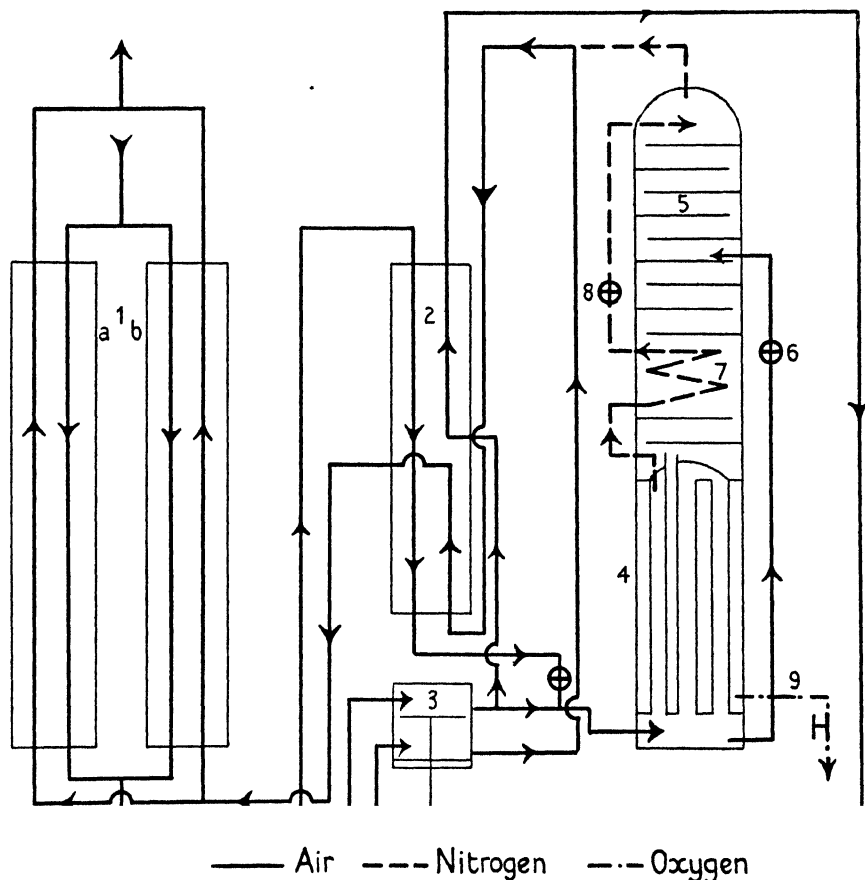


FIG. 114. Claude plant for liquid oxygen with double expansion engine and dephlegmator

by means of liquid reflux, expanded in the valve 8, and thereupon delivered at the top of the column.

This apparatus is rather complicated and somewhat less efficient than the Heylandt plant described under (5).

In recent years practical requirements and technical innovations have produced a further development in air separation, but by now, through lapse of patents and a partial merging of interests, it has become difficult to distinguish between French and German constructional elements.

Whereas for welding and many other purposes very pure oxygen is required, this is no longer the case when oxygen is used to further combustion in metallurgical processes. On the contrary, the 'rich air' industry has to fulfil a demand for mixtures containing only slightly more oxygen than atmospheric air, 45 per cent. oxygen in some cases and up to 70 per cent. in others. It has been found profitable to manufacture oxygen of about 98 per cent. purity and then to dilute this product with ordinary air. Since 'rich air' enters into competition with the atmosphere itself, which can be had free of charge, it is essential that the product be as cheap as possible.

The inventions which have enabled this demand to be satisfied are the cold accumulator and the turbine. The former has been described in some detail in Chapter III, and it was shown that, with accumulators replacing heat-exchangers, it is not possible to produce very pure products. However, this is not necessary in the 'rich air' industry.

In modern air-separating aggregates the turbine fulfils two objects. When used as a compressor it has a greater efficiency than the reciprocating engine, bringing down the factor with which theoretical power consumptions must be multiplied from 1.7 to about 1.3; and, used as an expansion engine, it brings the process nearer to the adiabatic curve and therefore gives rise to a greater refrigerating performance than the other types of expansion engine. Moreover, since no oil is required in a turbine, the difficulties of lubrication are automatically obviated, so that turbine expansion engines can be used to advantage at low temperatures.

Turbine compressors are difficult to construct for high working pressures; they are most suitable for work between 1 and 10 atm. They are therefore employed to the greatest advantage in large aggregates, in which the heat losses are relatively small and a comparatively low refrigerating performance is required. This is the case in the 'rich air' industry, which demands vast quantities of impure oxygen.

*No. 10.* Fig. 115 shows a diagram of a modern large-scale 'rich air' plant, which produces oxygen of 98 per cent. purity. The air is compressed to  $4\frac{1}{2}$  atm. in a turbine compressor 1 and cooled in two pairs of accumulators 2 and 3, which are fed with nitrogen and oxygen respectively. As was shown in Chapter III, these accumulators simultaneously remove moisture and carbon dioxide. The air is then separated in a double column of the ordinary Linde type. To cover heat leakage, a small quantity of nitrogen is withdrawn from the top of the lower column at 4, slightly heated with incoming air in an

exchanger 5, and then expanded in a turbine 6 to atmospheric pressure. The nitrogen then serves to cool a small current of air, compressed to 200 atm. and precooled with ammonia, which is thereupon expanded in a valve and introduced into the upper column.

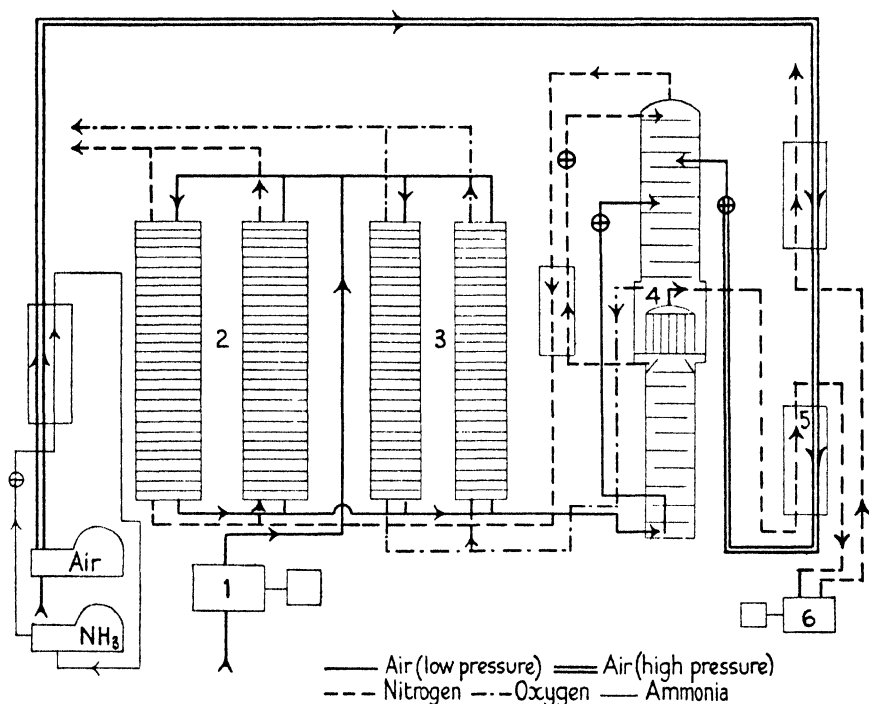


FIG. 115. Linde-Fränk plant for 98 per cent. gaseous oxygen. (Details of ammonia cycle and supplementary air circuit not shown)

This type of plant is made to produce up to 8,000 cub. m. (280,000 cub. ft.) of oxygen an hour. Its advantage is not merely that the power consumption is smaller than in the plants hitherto described, but that the cost of chemicals is very greatly reduced owing to the work of the accumulators.

In the following table the power consumption is given per 1,000 cub. ft. of oxygen, at 1 atm. pressure, as obtained in the various types of plant here described. The numbers in the first column correspond to the numbers used in this chapter. In the first line of the table the capacity of the plants is given in cubic metres of oxygen per hour, as these are the figures given in the catalogues, and a conversion to cubic feet would destroy the 'round' figures. It may be noted that 1 cub. m. is equal to 35.315 cub. ft. The values for the power consumption are taken

from the catalogues; in practice they will be somewhat different and will depend on the conditions in the factories and the skill of the staff.

TABLE 21. *Power Consumption in kilowatt-hours per 1,000 cub. ft. of Oxygen at 1 atm. in Various Plants*

Cub. m. O <sub>2</sub> per hr. .	10	15	20	25	30	40	60	80
Type								
1	48.3	46.2	46.2	..	44.1	44.1	..	..
2	..	33.6	..	..	29.4	..	29.4	29.4
3	..	..	..	..	..	..	..	..
4	..	..	..	..	..	..	..	..
7	..	..	..	26.2	..	24.1	..	23.0
10†	..	..	..	..	..	..	..	..

Cub. m. O <sub>2</sub> per hr. .	100	150	200	250	300	500	1,000	8,000
Type								
1	..	..	..	..	..	..	..	..
2	..	..	..	..	..	..	..	..
3	26.6	..	24.8	..	24.6	23.9	23.9	..
4	22.7	..	21.4	..	20.4	18.9	18.3	..
7	..	22.8	..	20.4	..	18.7	..	..
10†	..	..	..	..	15.1	..	..	12.7

† Refers to 98 per cent. oxygen.

The following Table 22, compiled by L. Meyer,† gives comparative figures for the cost of production of 98 per cent. oxygen in three plants. The first consists of three units, that together make 8,000 cub. m. of oxygen per hour (283,000 cub. ft. per hour) using cold accumulators. The second and third consist of one unit each, making 300 cub. m. (10,600 cub. ft.) per hour. No. 2 employs accumulators, while in No. 3 heat-exchangers are used. The oxygen is delivered at atmospheric pressure. The prices are quoted in German pfennigs.

TABLE 22. *Cost of Production of 98 per cent. Oxygen No. 1*

	Required	Pf. per cub. m. oxygen	% of total
Air . . . . .	45,000 cub. m./hr.	..	..
Chemicals . . . . .	1.5 kg./hr.	0.005	0.3
Lubricating oil . . . . .	2.4 kg./hr.	0.03	2.0
Water . . . . .	160 cub. m./hr.	0.04	2.6
Power . . . . .	3,600 kW.	0.90	58.8
Wages . . . . .	5 persons	0.075	4.9
Depreciation, 15% p.a. on .	2,000,000 RM.	0.48	31.4
	Total	1.53	

† L. Meyer, *Die Kosten Chemischer Operationen*, 1936.

## No. 2

	<i>Required</i>	<i>Pf. per cub. m. oxygen</i>	<i>% of total</i>
Air . . . . .	1,700 cub. m./hr.	..	..
Chemicals . . . . .	0.5 kg./hr.	0.05	1.4
Lubricating oil . . . . .	0.3 kg./hr.	0.11	3.0
Water . . . . .	11 cub. m./hr.	0.07	2.0
Power . . . . .	160 kW.	1.06	29.4
Wages . . . . .	2 persons	0.65	18.0
Depreciation, 15% p.a. on . . . . .	270,000 RM.	1.66	46.2
	Total	3.60	

## No. 3

	<i>Required</i>	<i>Pf. per cub. m. oxygen</i>	<i>% of total</i>
Air . . . . .	1,700 cub. m./hr.	..	..
Chemicals . . . . .	1.6 kg./hr.	0.18	4.4
Lubricating oil . . . . .	0.3 kg./hr.	0.11	2.7
Water . . . . .	18 cub. m./hr.	0.12	2.9
Power . . . . .	200 kW.	1.33	32.3
Wages . . . . .	2 persons	0.65	15.8
Depreciation, 15% p.a. on . . . . .	270,000 RM.	1.72	41.9
	Total	4.11	

The relative importance of the various items in the production of pure compressed gaseous oxygen in cylinders may be inferred from the following figures for a Russian factory, quoted by Pavlov.†

TABLE 23. *Costs of Production of 1 cub. m. of Compressed Oxygen in Cylinders (High Purity)*

Power . . . . .	1.39 kWh. per cub. m. . . . .	0.1340 Rbl.
Caustic . . . . .	0.021 kg. per cub. m. . . . .	0.0064 Rbl.
Wages . . . . .	0.031 men hours . . . . .	0.0430 Rbl.
All other items‡ . . . . .	. . . . .	0.1200 Rbl.
	Total	0.3034 Rbl.

† K. F. Pavlov and M. P. Malkov, *Refrigeration in Chemical Industry* (Russian), Leningrad, 1937, p. 206.

‡ This includes all other forms of power, water, maintenance, wages of office personnel, social insurance, current repairs, and depreciation.



## VIII

### THE SEPARATION OF AIR (3)

#### EFFECT AND EFFICIENCY OF PLATE COLUMNS

##### 1. The effect of plates with mixed liquid

IN Chapter VI it was shown how, under certain simplifying assumptions, the number of plates theoretically required in a rectifying column, in order to produce a specified degree of separation, could be computed. The calculations were carried out on the  $(h, x)$  diagram with the help of the concept of *equivalent currents*. The advantage of the  $(h, x)$  diagram was that it enabled us to determine simultaneously the quantity of heat transferred at various points of the apparatus.

In engineering practice it is often found expedient to consider the changes in concentration, brought about on the plates of a column, without at the same time taking the heat transfer into account. For this purpose it is useful to employ a figure that is rather simpler than the  $(h, x)$  diagram. The *composition diagram*, in which the composition of the vapour is plotted as a function of the composition of the liquid, actually gives us less information than the  $(h, x)$  diagram; but it is met with so frequently and has been referred to so often in the literature that our presentation would be incomplete if we did not consider it.

If, for the case of oxygen–nitrogen mixtures, we plot the composition  $z$  of a vapour as a function of the composition  $x$  of a liquid with which it is in equilibrium, we obtain the curve shown in the composition diagram of Fig. 116. If  $x$  and  $z$  are measured in percentages of nitrogen, the curve is convex towards the ordinate axis, since there is always more nitrogen in the vapour than in the corresponding liquid.

Now in a certain horizontal section of a rectifying column of the type heretofore described, let  $y$  be the nitrogen concentration of a vapour in contact with a liquid containing  $x$  per cent. of nitrogen. Since, as we know, this vapour is not in equilibrium with the liquid, it will not be represented by a point on the curve in Fig. 116.

To determine  $y$  as a function of  $x$ , we must go back to the argument of Chapter VI. Here we showed that, if  $L$  and  $G$  are the liquid and vapour phases respectively in a certain horizontal section of the column, the equation

$$L - G = F = \text{const.} \quad (1)$$

held throughout the column, provided that no substances were introduced or withdrawn on the way. This equation was to be considered

as an abbreviation for the three balance equations of mass, composition, and enthalpy:

$$\left. \begin{aligned} m_L - m_G &= m_F, \\ m_L x_L - m_G x_G &= m_F x_F, \\ m_L h_L - m_G h_G &= m_F h_F. \end{aligned} \right\} \quad (2)$$

Using the same arguments, it can be shown that the products  $m_L \lambda_x$  and  $m_G \lambda_y$  are constant throughout the column, where  $\lambda_x$  and  $\lambda_y$  are the

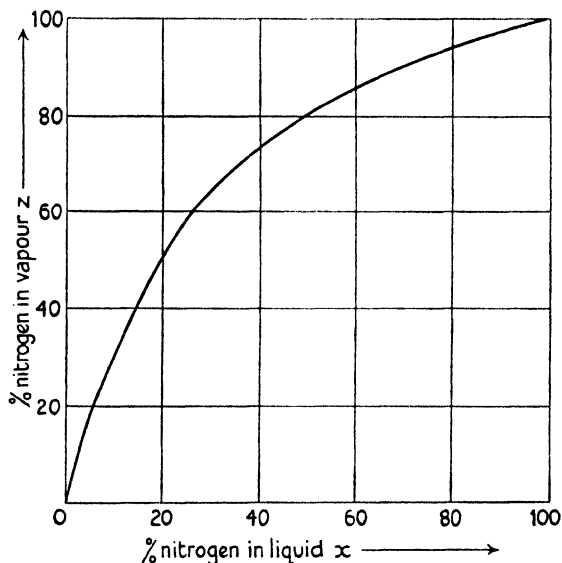


FIG. 116. Composition curve of oxygen-nitrogen mixtures

latent heats of evaporation, at constant pressure and constant composition (see Chapter IV, § 3), of liquids with the compositions  $x$  and  $y$  respectively.

This can also be proved from equations (2) directly as follows. Putting  $x_L = x$  and  $x_G = y$ , we can write equations (2) in the form

$$\left. \begin{aligned} m_L - m_G &= A, \\ m_L x - m_G y &= B, \\ m_L h_L - m_G h_G &= C, \end{aligned} \right\} \quad (3)$$

where  $A$ ,  $B$ , and  $C$  are constants. Neglecting heats of mixing, which are unappreciable for mixtures of oxygen and nitrogen, we can express the enthalpies of the mixtures in terms of the enthalpies of the pure components as follows:

$$\left. \begin{aligned} h_L &= x h_{1L} + (1-x) h_{2L}, \\ h_G &= y h_{1G} + (1-y) h_{2G}, \end{aligned} \right\} \quad (4)$$

where the subscripts 1 and 2 refer to the components.  $h_{1L}$  and  $h_{2L}$  can be replaced by the latent heats of the pure components, so that the first of the equations (4) can be written

$$h_L = x(h_{1G} - \lambda_1) + (1-x)(h_{2G} - \lambda_2). \quad (5)$$

Inserting (4) and (5) in the last of equations (3), we obtain

$$m_L\{x\lambda_1 + (1-x)\lambda_2\} = (m_L x - m_G y)h_{1G} + \{m_L(1-x) + m_G(1-y)\}h_{2G} - C, \quad (6)$$

or, using the first two equations of (3),

$$m_L \lambda_x = B h_{1G} + (A - B) h_{2G} - C, \quad (7)$$

where  $\lambda_x$  is the latent heat of evaporation of a liquid with the composition  $x$ . Inserting the values of the constants  $A$ ,  $B$ , and  $C$ , we can write (7) in the form

$$m_L \lambda_x = m_F(h_{FG} - h_F), \quad (8)$$

where  $h_{FG}$  is the enthalpy of a saturated vapour of the composition of  $F$ . All the terms on the right of (8) are constants throughout the column. By eliminating  $h_{1G}$  and  $h_{2G}$  instead of  $h_{1L}$  and  $h_{2L}$  in equation (4), a similar relation can be obtained for  $m_G \lambda_y$ .

We have thus proved that  $m_G \lambda_y$  and  $m_L \lambda_x$  are constants throughout the column. Since, in an air column, the nitrogen concentration increases towards the top, and since the latent heat of evaporation of nitrogen is slightly less than that of oxygen, it follows that  $m_G$ , the amount of vapour passing a horizontal section of the column in a specified time, is greater at the top than at the bottom. But since the latent heats differ but slightly (1,632 cal./mole for oxygen, and 1,337 cal./mole for nitrogen) the change of  $\lambda$  can frequently be neglected. For not too accurate calculations we can thus simply put  $m_G = \text{const.}$  and similarly  $m_L = \text{const.}$  In this case we can compute the composition of liquid and vapour on any plate as follows with the help of equations (3).

For any two adjacent plates 1 and 2 these equations give us

$$m_{L_1} - m_{G_1} = m_{L_2} - m_{G_2},$$

$$m_{L_1} x_1 - m_{G_1} y_1 = m_{L_2} x_2 - m_{G_2} y_2,$$

or, since  $m_{L_1} = m_{L_2} = m_L$  and  $m_{G_1} = m_{G_2} = m_G$ ,

$$m_L(x_1 - x_2) = m_G(y_1 - y_2);$$

whence

$$y_2 - y_1 = \frac{m_L}{m_G}(x_2 - x_1), \quad (9)$$

or, for any point in the column,

$$y = y_1 - x_1 \frac{m_L}{m_G} + x \frac{m_L}{m_G}, \quad (10)$$

where  $x_1$  and  $y_1$  are the compositions of liquid and vapour at one end of the column or at a specified horizontal section thereof.

The composition  $y$  of vapour in contact with liquid of composition  $x$  is thus given by the points of a straight line. If the composition of liquid and vapour at both ends of the column is given, the straight line passes through, and is therefore defined by, the points marking these compositions.

If we write equation (9) in the form

$$\frac{m_L}{m_G} = \frac{y_2 - y_1}{x_2 - x_1} \quad (11)$$

and suppose the indices 1 and 2 to refer to the two ends of the column, we can determine the amount of liquid reflux  $m_L$  required to produce a specified rectifying effect on a given quantity  $m_G$  of gas of known composition.

If we do not neglect the differences of the latent heats, equation (8) gives us for two neighbouring plates  $n$  and  $n+1$

$$m_{G_{n+1}} = m_{G_n} \frac{\lambda_{y_n}}{\lambda_{y_{n+1}}}, \quad (12)$$

and, with the help of equations (3), we obtain

$$x_{n+1} = \frac{m_{L_n} x_n + m_{G_{n+1}} y_{n+1} - m_{G_n} y_n}{m_{L_n} + m_{G_{n+1}} - m_{G_n}}. \quad (13)$$

If we put  $y_{n+1} = z_n$ , i.e. assume complete equilibration on each plate, we can calculate from (12) and (13) the composition of liquid and vapour on each plate successively. Equation (10) follows from (13) if we put  $m_{G_{n+1}} = m_{G_n}$ , or, which comes to the same thing,  $\lambda_{y_n} = \lambda_{y_{n+1}}$ .

If we take the differences in latent heats into consideration, the straight line giving  $y$  as a function of  $x$  will be slightly curved. For the case of oxygen-nitrogen mixtures, it is generally assumed to be straight, and is known as the *working line*.

Now suppose the working line  $y(x)$  of a column to be known from the specified conditions at the ends, and the curve  $z(x)$  to be determined from the equilibrium diagram. Let  $y_n$  be the composition of a vapour on entering the  $n$ th plate from below, in contact with a liquid  $x_n$  leaving the same plate (see Fig. 117). Then the point  $(x_n, y_n)$  lies on the working

line. On passing through the plate, the vapour will approach equilibrium with the liquid  $x_n$ . If equilibrium is actually attained, the vapour will leave the plate  $n$  with a composition  $z_n$ , the point  $(x_n, z_n)$  being on the equilibrium curve. The distance  $z_n - y_n$ , the *distance from equilibrium* of the vapour on entering the plate, is at the same time the maximum change in composition which the vapour can undergo on

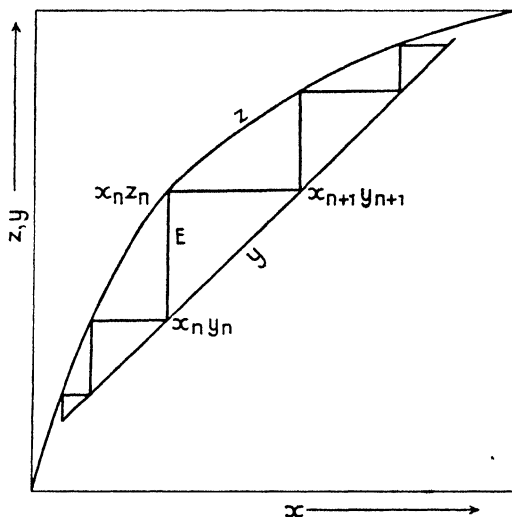


FIG. 117. Composition curve and working line.  
Method of determining the number of plates

passing through the plate. We shall call  $z_n - y_n$  the *theoretical effect*  $E$ , or simply the *effect* of the  $n$ th plate. The ratio of the actual change of composition, undergone by the vapour on passing through the plate, to this maximum change will be termed the *efficiency*  $\epsilon$  of the plate.

The fact that the effect or maximum change in composition is equal to the distance from equilibrium  $z_n - y_n$  on entering is not a general law, but is due to the particular type of plate that we are here discussing, i.e. a plate on which the composition of the liquid is the same at all points. We shall see later that plates may be designed for which  $E$  is considerably greater than  $z_n - y_n$ . But for the moment we shall keep to plates of the kind already described.

Now if the efficiency  $\epsilon$  of our plate is equal to unity, the vapour will leave it with a composition  $z_n$  and proceed to the  $(n+1)$ th plate above. Thus  $z_n = y_{n+1}$ , and  $(x_{n+1}, y_{n+1})$  will again be a point on the working line, and it can be found by drawing a horizontal line from  $z_n$  (see Fig. 117). In this way we can draw a series of steps, which will give

us the number of plates needed, assuming always that  $\epsilon = 1$ , and the composition of liquid and vapour on each plate can be determined. The result will probably not be a whole number of plates, but this cannot be expected. The theoretical number of plates, obtained according to this method, is usually defined as the nearest whole number exceeding the graphical result.

The number of plates obtained will be nearly the same as that resulting from the method described in Chapter VI, but it will be slightly less accurate, as it assumes the constancy of  $m_G$  and  $m_L$  throughout the column. The principal advantage of this method, as against that used in Chapter VI, is that it is based on the equilibrium curves alone and does not require the knowledge of  $h$ .

The next approximation for computing the number of plates required is to assume an efficiency  $\epsilon < 1$ , which may be taken from past experience, and to suppose that this  $\epsilon$  is the same for all the plates of the column. In this case, the practical change in composition, undergone by a vapour in passing through the  $n$ th plate, will be given by the equation

$$y_{n+1} - y_n = \epsilon(z_n - y_n). \quad (14)$$

The point  $(x_{n+1}, y_{n+1})$  will therefore lie on the working line somewhat lower than  $(x_{n+1}, z_n)$ . It may thus be connected with  $(x_n, z_n)$  by a straight line that is not horizontal, but slopes downwards from left to right, as in Fig. 118. We can show that all these lines in the staircase so obtained have the same slope. Consider two neighbouring plates and the corresponding diagram and draw the two horizontal lines, as shown in the figure. Then the triangles  $ACD$  and  $DFG$  are similar, since the corresponding sides are all parallel. Therefore

$$AC/DF = CD/FG.$$

But, according to our assumption,

$$AC/AB = DF/DE = \epsilon.$$

Therefore

$$AC/BC = DF/EF;$$

whence

$$AC/DF = BC/EF = CD/FG.$$

Therefore, since the angles at  $C$  and  $F$  are equal, the triangles  $BCD$  and  $EFG$  are similar. Therefore, since  $BC$  and  $EF$  are parallel, it follows that  $BD$  is parallel to  $EG$ .

If the two ends  $P$  and  $Q$  of the working line are given, as well as the efficiency  $\epsilon$ , we can obtain the common slope of all the steps as follows (see Fig. 118): Describe a vertical straight line  $PR$  so that  $PR = QS/\epsilon$ . Then  $RQ$  has the slope of the steps. This may be proved

as follows: Let  $TV$  be the first step, and let  $QR$  be parallel to  $TV$ . Then, since the triangles  $RQP$  and  $TVP$  are similar, and  $VL$  is parallel to  $QM$ ,

$$QS/PR = MP/PR = PL/PT = \epsilon.$$

Thus  $TV$  has the correct slope of the steps if it is parallel to  $QR$ .

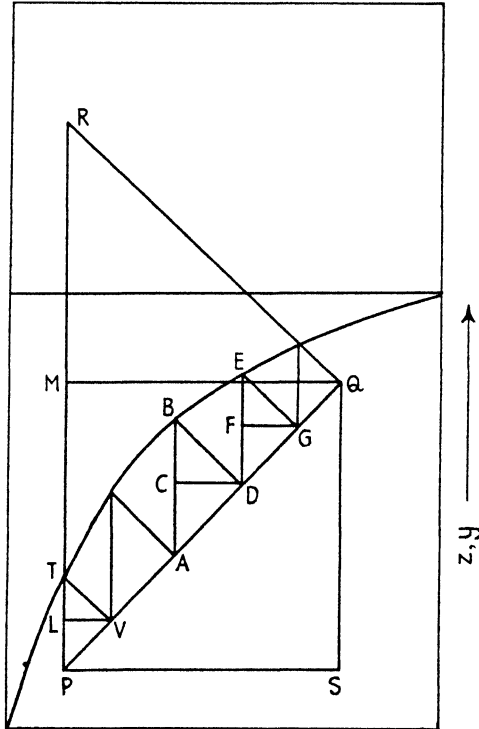


FIG. 118. Method of determining the number of plates for a constant efficiency less than unity

The above arguments are valid only for a single column to which mixture is delivered at the top or bottom. If liquid or vapour is introduced or withdrawn at some point in the middle of the column, the working line will show a break at that point. There will be two working lines, one for the part of the column below the inlet or outlet, and the other for the upper part. The two lines will meet at an angle at this point.

Consider a single column with an evaporator and a condenser, to which liquid is introduced at the middle; and let us suppose, for the sake of convenience, that the column has so many plates that both

products are practically pure. Then the lowest point of the lower working line and the highest point of the upper working line will practically coincide with points on the equilibrium curve corresponding to 0 and 100 per cent. respectively. We may now further assume that the liquid entering in the middle is at its boiling-point and is introduced at a point of the column at which the liquid reflux has the same composition as the liquid entering.

With these assumptions it can be shown that the amount of reflux required will be a minimum if the composition of the vapour at the point of entry is such as to be in equilibrium with the liquid entering the column, in which case the two working lines will meet at the equilibrium curve. For, according to equation (11),

$$\frac{m_L}{m_G} = \frac{y_2 - y_0}{x_2 - x_0}, \quad (15)$$

where 0 and 2 refer to the inlet and the top of the column respectively. According to our assumption,  $x_2 = y_2 = 1$ , so that

$$\frac{m_L}{m_G} = \frac{1 - y_0}{1 - x_0}. \quad (16)$$

Therefore, the greater  $y_0$ , the smaller  $m_L$  will be. But the maximum value of  $y_0$  is obviously  $z_0$ , the composition of a gas in equilibrium with  $x_0$ .

A minimum of  $m_L$  means a minimum of condensation in the condenser and therefore a minimum of refrigeration at that point. It is therefore economical to condense as little reflux as possible. On the other hand, the diagram here considered entails an infinite number of plates. In practice a compromise will be sought that will keep the required number of plates down to an acceptable figure without unduly increasing the reflux and with it the consumption of energy. This means that (a) the products will not be perfectly pure, and (b) the vapour at the inlet will contain less of the more volatile component than is in equilibrium with a liquid of the composition  $x_0$ .

## 2. Plates with inhomogeneous liquid

Up till now we have assumed that the *effect* of a rectifying plate, i.e. the maximum change in composition, undergone by a vapour on passing through a plate, is equal to the difference in composition  $z - y$  between the vapour entering the plate and a vapour in equilibrium with the liquid leaving it. The 'staircase method' of determining the required number of plates, as well as the method discussed in



Chapter VI, was based on this assumption, which, until recently, was thought to be universally valid.

Now all the arguments which led us to this view are themselves based on another assumption, which is that the liquid on a plate is homogeneous, i.e. that its composition is the same at all parts of the plate. In plates of older pattern this was always brought about by so designing them that the liquid was violently stirred by the bubbles of vapour passing through it and had itself no definite direction of flow. It was, in fact, more or less tacitly assumed that this arrangement would lead to the greatest effect of a plate, i.e. would produce the greatest change of composition in a vapour passing through it.

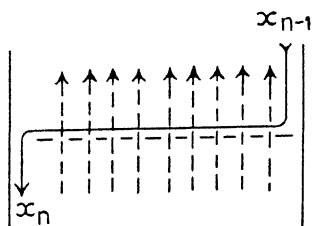


FIG. 119. Plate on which the liquid is not stirred and has a definite direction of flow.

Some years ago Hausen† and Kirschbaum‡ showed theoretically that this assumption is untrue, and in modern separating plants a type of plate is employed which has a greater effect than those hitherto described.

Suppose a plate to be so designed that the liquid on it has a definite direction of flow and that the liquid in one part does not mix with that in another part of the plate. Let the composition of the liquid arriving on the plate be  $x_{n-1}$ , and that of the liquid leaving  $x_n$  (see Fig. 119). The composition of the liquid will change continuously from  $x_{n-1}$  to  $x_n$  as it passes over the plate. We assume that the plate is perforated in the usual way and that the vapour passes up through the holes as in the older type. Unless particular precautions are taken, the vapour entering the plate from below will also vary in composition from point to point, owing to its past interaction with liquid on lower plates.

Let  $y_n$  be the mean composition of the vapour below the plate. Then  $(x_n, y_n)$  is a point on the working line, which is defined as before. Now since  $x_n$  is the composition of the liquid leaving the plate, the mean composition  $x'_n$  of the liquid on the plate will be greater than  $x_n$ . Therefore the mean composition  $z'_n$  of a vapour in equilibrium with a liquid on the plate will be greater than  $z_n$ , the composition of a vapour in equilibrium with  $x_n$ . The maximum mean change of composition,

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, 7, 177 (1936).

‡ E. Kirschbaum, *ibid.* 5, 245 (1935); E. Kirschbaum and E. Quade, *ibid.* 8, 63 (1937).

|| Greater because we agreed to measure compositions by the concentration of the more volatile component, in this case nitrogen.

incurred by the vapour in passing through the plate, will now be  $z'_n - y_n$ , and this is greater than  $z_n - y_n$ . Now  $z'_n - y_n$  is the effect of the plate, as it is the maximum value of  $y_{n+1} - y_n$ .

To make this clear, consider again the working line in conjunction with the equilibrium curve  $z(x)$ . The latter, in oxygen-nitrogen mixtures, is very steep at low values of  $x$  and becomes flatter as  $x$  approaches

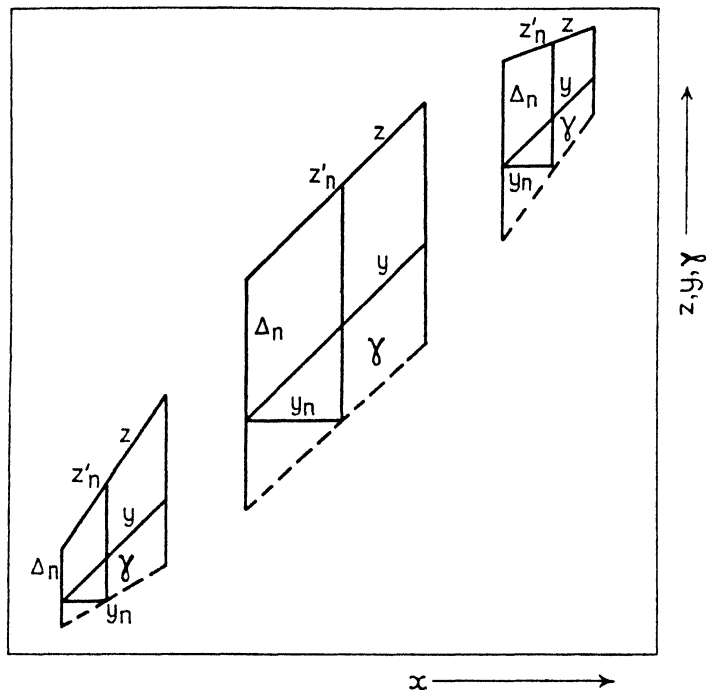


FIG. 120. Effect of plates with inhomogeneous liquid. Schematical portions of equilibrium curve ( $z$ ), working line ( $y$ ), and curve giving composition of vapour entering plate from below ( $\gamma$ )

unity. In Fig. 120 part of the equilibrium curve is shown schematically as a broken line consisting of three parts. The first is steeper than the working line, the second is parallel to it, and the third is flatter.

The steeper the equilibrium curve, as compared with the working line, the greater  $z'_n$  will be, as compared with  $z_n$ , for a given value of  $x'_n > x_n$ , and thus the greater will be the effect of the plate.

Now let  $b = dz/dx$ , the slope of the equilibrium curve at the point  $x$ . The slope of the working line is  $m_L/m_G$ . If we now put

$$bm_G/m_L = \beta, \quad (17)$$

the effect of the new plate will be the greater, as compared with that of the old plate, the greater  $\beta$ .

Let the effect of the old plate  $z_n - y_n = \Delta_n$ . (18)

Then, according to Hausen, the expression

$$\phi = \frac{y_{n-1} - y_n}{\Delta_n} \quad (19)$$

is called the *equilibration ratio*. If complete equilibrium is reached between liquid and vapour, i.e. if the efficiency of the plate is equal to unity,  $y_{n-1} = z'_n$  and

$$\phi = \frac{\text{effect of new plate}}{\text{effect of old plate}}.$$

In Fig. 120 the dotted line shows the actual composition  $\gamma$  of the vapour, as it varies from place to place.  $y_n$  is the mean value of  $\gamma$  for a certain plate.  $z - \gamma$  is the effect of a given point on the plate, and  $z'_n - y_n$  is the effect of the plate as a whole.

In the lower part of Fig. 120, in which  $\beta > 1$ , we see that  $z - \gamma$  increases with increasing values of  $x$ ; in the central part, in which  $\beta = 1$ ,  $z - \gamma$  is a constant; in the top portion, where  $\beta < 1$ ,  $z - \gamma$  decreases as  $x$  increases. But in all cases  $z'_n - y_n > \Delta_n$ , i.e.  $\phi > 1$ .

In order to determine quantitatively the effect of a plate, we must know the actual composition  $\gamma$  of the vapour as a function of  $x$ . In general  $\gamma$  will vary from point to point of the plate, except at the plate immediately above or below the inlet, at which the vapour will be homogeneous. Hausen has shown that the farther away we are from the inlet the nearer  $\gamma$  approaches a definite limiting curve. Moreover,  $\gamma$  will also depend on whether the liquid flows in the same direction on each plate or whether it changes its direction from plate to plate. The greatest values of  $z'_n - y_n$  are obtained when the direction of flow is uniform.

Fig. 121 shows the equilibration ratio  $\phi$  for various cases as a function of  $\beta = (m_G/m_L)b$ . The upper curves were computed for an efficiency  $\epsilon = 1$ , the lower curves for  $\epsilon = 0.5$ . It will be noted that, for  $\beta = 1$ , i.e. when the equilibrium curve is parallel to the working line, case (a) gives  $\phi = 2$  and case (b)  $\phi = 1.5$ , when  $\epsilon = 1$ . In this case, a plate of the new type has an effect twice as great or one and a half times as great as an old plate, according as the direction of flow of the liquid is the same on each plate or varies from one plate to the next.

In a plant for separating air, it is clear that the effect of plates near the bottom of the column will be much greater than near the top, as the equilibrium curve is much steeper in the region of high oxygen concentrations. This is illustrated in Fig. 122, which shows  $\phi$  as a

function of the position of the plate in the top half of a double column for separating air. The abscissae are nitrogen concentrations, so that the right-hand side of the figure corresponds to the top of the upper column.

On the basis of rather intricate calculations, Hausen† gives the following approximate graphical method for determining the change of

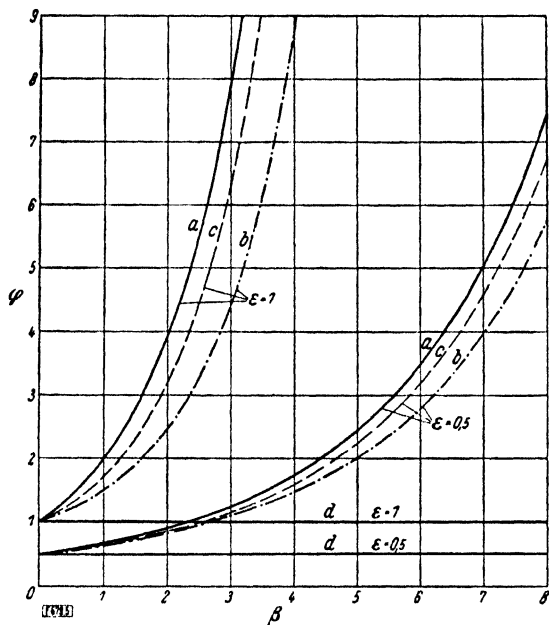


FIG. 121. Equilibration ratio  $\phi$  as a function of  $\beta = \frac{dz}{dx} \frac{m_g}{m_L}$  for efficiencies  $\epsilon = 1$  and  $0.5$

- a Direction of liquid flow the same on all plates; no stirring
- b Direction of liquid flow alternating from plate to plate; no stirring
- c Vapour stirred and homogeneous
- d Vapour and liquid homogeneous

composition undergone by a vapour in passing through a plate, on which the liquid has a definite direction of flow and on which stirring is eliminated. Hausen supposes that the efficiency  $\epsilon$  of the plates is known. He then introduces two magnitudes  $\Phi$  and  $A$  as follows:

For plates on all of which the direction of flow is the same

$$\Phi = \frac{2\epsilon}{2-\epsilon}, \quad A = \frac{1}{3}\Phi. \quad (20)$$

† H. Hausen, *Actes du VII<sup>ème</sup> Congrès International du Froid*, La Haye, 1936, vol. i, p. 349.

For plates on which the direction of flow alternates

$$\Phi = \frac{2}{3} \frac{\epsilon(2-\epsilon)}{1+(1-\epsilon)(2-\epsilon)}, \quad A = \Phi \frac{4}{15} \frac{5(1-\epsilon)+\epsilon^2}{(2-\epsilon)^2}. \quad (21)$$

The change in composition of a vapour passing through a plate can then be determined in a number  $k$  of stages. The greater  $k$ , the greater the accuracy, but usually  $k = 2$  or  $3$  will be sufficient.

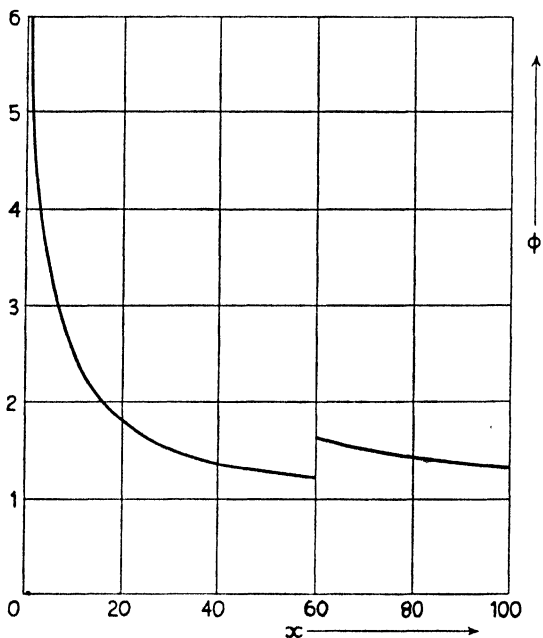


FIG. 122. Equilibration ratio  $\phi$  as a function of the composition of the liquid  $x$  in the upper part of a double air column

On a separate graph (Fig. 123) draw a vertical line of unit length on an arbitrary scale, beginning from a zero point  $O$ . From  $O$  draw a straight line parallel to the working line and cut off lengths  $OQ$  and  $OP$  to right and left of  $O$ , the vertical projections of which are equal to

$$\frac{\Phi}{2k}(1+kA) \quad \text{and} \quad \frac{\Phi}{2k}(1-kA) \quad \text{respectively.}$$

Then join  $PR$  and  $QR$ . If we now introduce between the working line and the equilibrium curve a series of straight lines alternately parallel to  $PR$  and  $QR$  (see Fig. 123),  $k$  such pairs of straight lines will give us the change in composition of a vapour passing through the plate.

For the case of  $\epsilon = 1$ ,  $\Phi$  for uniform motion is 2 and for alternate

motion  $2/3$ , and the corresponding values of  $A$  are  $1/3$  and  $8/45$  respectively. The method will then give the 'effect' of the plate.

The construction is exact for  $\beta = 1$  and is fairly accurate when  $\beta$  is not far removed from unity. But it assumes that the influence of the

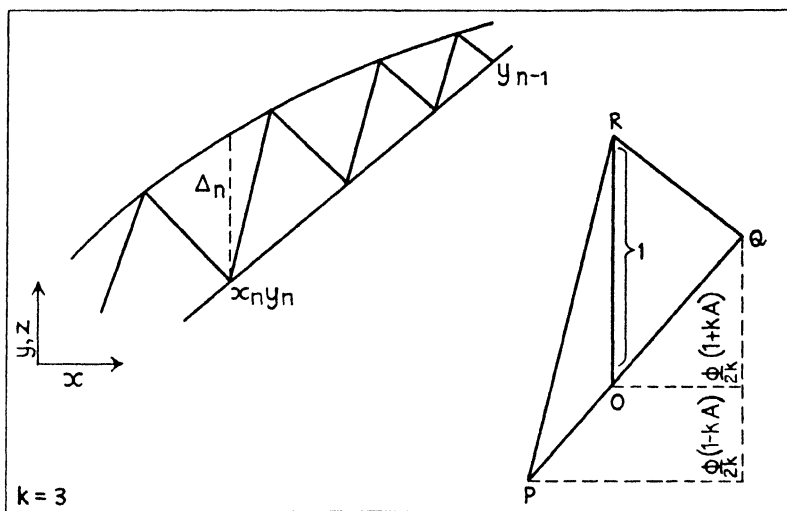


FIG. 123. Graphical method of determining the effect of a plate with inhomogeneous liquid

homogeneous vapour at the inlet is negligible. For the plate immediately above the inlet we can use the same construction with

$$\Phi = e^{-\epsilon} - 1, \quad A = 1 - 2 \frac{1 - (1 - \epsilon)e^{-\epsilon}}{(e^{-\epsilon} - 1)^2}. \quad (22)$$

A method devised for the same purpose by Kirschbaum and Quade† obviates some of the mathematical difficulties by a more graphical treatment and at the same time eliminates the approximations. However, for practical purposes it is slower than Hausen's simple construction.

Kirschbaum considers the limiting case of  $\epsilon = 1$ , and sets out to determine the composition of a vapour leaving various points of a plate when that of the vapour and liquid entering the plate is known. The liquid is assumed to flow along the plate in a definite direction, and stirring is eliminated.

To obtain the required equation, suppose the plate to be divided into  $n$  equal parts, which are traversed by the liquid successively. If

† Loc. cit.

$m_L$  is the total amount of liquid and  $m_G$  the total amount of vapour traversing the plate in a given time, then each of the  $n$  parts of the plate is traversed by  $m_L$  moles of liquid and  $m_G/n$  moles of vapour. Let  $x_{k-1}$  and  $x_k$  be the composition of the liquid respectively entering and leaving the  $k$ th part of the plate, and let  $y_k$  and  $y'_k$  be the composition of the vapour before and after traversing this section. Then the balance of the component whose concentration is measured by  $x$  reads:

$$\frac{m_G}{n}(y'_k - y_k) = m_L(x_k - x_{k-1}), \quad (23)$$

or 
$$\frac{y'_k - y_k}{x_k - x_{k-1}} = n \frac{m_L}{m_G}. \quad (24)$$

Now let  $t_k = k/n$ , so that  $t_k - t_{k-1} = 1/n$ . If we introduce this in (23), we obtain

$$\frac{x_k - x_{k-1}}{t_k - t_{k-1}} = \frac{m_G}{m_L}(y'_k - y_k). \quad (25)$$

If we now let the number of intervals tend to infinity, (25) will read

$$\frac{dx}{dt} = \frac{m_G}{m_L}(y' - y). \quad (26)$$

This equation gives us the relation between the composition of the liquid as a function of its position on the plate and the corresponding composition of the vapour above and below the plate.

In the general case this equation is not easy to solve, though a graphical solution is possible. But in one case the solution is very simple, and that is when the vapour phase is homogeneous. Then  $y$  is a constant for a given plate, and the variables may be separated. We then have

$$\int_{x'}^{x''} \frac{dx}{y' - y} = \frac{m_G}{m_L} t. \quad (27)$$

$x'$  and  $x''$  are the respective compositions of the liquid when it leaves and enters the plate.

To see how this solution may be used in practice, let us consider part of a column for separating air. We shall suppose that the vapour phase is homogeneous but the liquid on the plates is not. Let the pressure be 1 atm. The column is to produce 95 per cent. nitrogen at the top, and the amount of liquid reflux is to be four times as great as the amount of nitrogen leaving the column. The column is assumed to have a condenser at the top, which condenses all the nitrogen. In this case, the composition of liquid and vapour at the top of the column will be identical.

In Fig. 124 the equilibrium curve  $EC$  is shown together with the working line  $WL$ , which may be obtained from equation (10), assuming that  $m_L/m_G = 4/5$  and that, at  $x = 0.95$ ,  $y = 0.95$  (point 1). Now consider a plate of the type described, the liquid leaving which is known

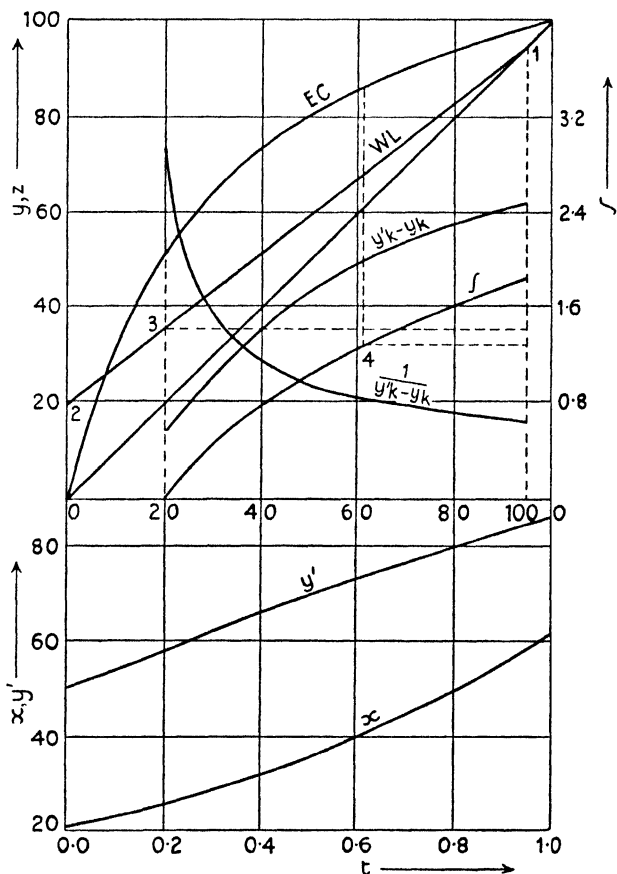


FIG. 124. Graphical method of determining the composition of liquid and vapour at any point of a plate with inhomogeneous liquid when the vapour entering the plate is homogeneous

to contain, say, 20 per cent. nitrogen. This gives us point 3 on the working line in Fig. 124, and shows us that the vapour entering the plate will contain 36.2 per cent.  $N_2$ . Assuming complete equilibrium to be reached between vapour and liquid at each point, we can now determine  $y' - y$  as a function of  $x$  for all points to the right of 3 by simply plotting the vertical distances from the equilibrium curve to the horizontal straight line  $y = 36.2$  per cent.  $N_2$ . This gives us the curve



$y'-y$ , also plotted in Fig. 124, from which we may determine the curve  $1/(y'-y)$ . Finally, we can obtain a curve  $\int_x^x dx/(y'-y)$  from a series of areas  $dx/(y'-y)$ , which are the result of multiplying suitably chosen small intervals  $dx$  with the corresponding values of  $1/(y'-y)$ . According to equation (27), these integrals must be equal to  $5t/4$ . This last curve is marked  $\int$  in Fig. 124.

For  $t = 1$ ,  $x$  must be equal to  $x''$  and the integral equals  $5/4 = 1.25$ . The curve attains this value at an abscissa  $x'' = 61$  per cent.  $N_2$  (point 4). This will therefore be the composition of the liquid entering the plate. Similarly, half-way across the plate,  $t = 0.5$ , and the integral is  $0.5 \times 1.25 = 0.625$ . This gives  $x_t = 36$  per cent.  $N_2$ . In this way the composition  $x$  of the liquid may be determined at every point of the plate.

Since complete equilibration is assumed, the composition  $y'$  of the vapour leaving the plate at each point will be given by the ordinate of the equilibrium curve immediately above the corresponding value of  $x$ . The two curves are shown in the lower part of Fig. 124.

Plates on which the liquid is maintained inhomogeneous and made to flow in a definite direction may be designed in various ways. In one of the most popular forms the liquid is made to flow along an annular surface, which has a vertical partition near the point at which the liquid is introduced. The partition causes the liquid to flow in one direction only, until it comes to the outlet, from which it is delivered on to the next plate. Evidently, by a suitable distribution of the partitions, the liquid may be constrained to flow in the same sense around each plate, or it may be made to change its direction from one plate to another.

### 3. Equilibration of liquid and vapour

We have seen that the change in composition, undergone by a vapour in traversing a plate, can be expressed as the product of the effect  $E$  of the plate and a factor  $\epsilon$  called the efficiency. In the last two sections it was shown how the effect of a plate may be determined and how it may be increased by appropriate designing. But up till now the efficiency has figured as a known and constant quantity, which was carried in the equations without comment, and on the numerical value of which no light was shed. It is a fact that, in text-books and original publications, very much more attention has been paid to effect than to efficiency. Though much is known as to how a change in design may

alter the effect of a plate, little thought has been given as to how this may influence its efficiency. Since the property of a plate which interests us most, the actual change in composition that it brings about, is equal to the product of effect and efficiency, an increase in the one may quite well be counteracted by a decrease in the other.

The effect of the plate is the change in composition that would be produced on a plate if the vapour leaving it were indeed in equilibrium with the liquid at the particular point. The efficiency tells us how far this equilibrium is actually attained.

The vagueness with which efficiency is generally treated is due to the considerable mathematical difficulties inherent in determining it. These difficulties, which were openly faced and, in part at least, overcome by Bošnjaković,<sup>†</sup> consist in the fact that every equilibration process between a binary liquid and its vapour comprises the simultaneous transfer of heat and matter from one phase to another. It follows from this that neither diffusion equations, based on differences of composition alone, nor equations of heat transfer, based only on differences of temperature, can give a complete account of the phenomena.

On the plates of a column the liquid is continually traversed by bubbles of vapour, which, at the moment when they enter the liquid, are not in equilibrium with it. We wish to elucidate what factors are at work in promoting equilibration, and what is the specific influence of each factor. Such factors may be the size of individual bubbles, their velocity or, which comes to the same thing, the time that they spend in contact with the liquid, their composition on entering the plate and the composition they would have if they were in equilibrium with the liquid, their temperature and the temperature of the liquid, etc.

Though we cannot here give a complete solution of the problem, we shall follow Bošnjaković's reasoning as far as is consistent with the scope of this book, and endeavour to draw some practical conclusions.

If a binary liquid be in contact with a vapour consisting of the same components, molecules of both kinds will be continually escaping from and condensing upon the liquid surface. These two phenomena may be termed *evasion* and *invasion* respectively. The amounts of the components 1 and 2 passing out of the liquid through unit surface in the time  $dt$  may be written

$$dm_1^\beta = \beta_1 x_1 dt, \quad dm_2^\beta = \beta_2 x_2 dt, \quad (28)$$

<sup>†</sup> F. Bošnjaković, *Technische Mechanik und Thermodynamik*, **1**, 358 (1930); *Forschung auf dem Gebiet des Ingenieurwesens*, **3**, 145 and 213 (1932). M. Ruhemann, *Physica*, **4**, 1157 (1937).

where  $x_1$  and  $x_2$  are the concentrations of the two components and  $\beta_1$  and  $\beta_2$  are known as *evasion coefficients* and may depend on temperature and composition of the liquid and on its state of motion.

In the same way, the amount of each component entering the liquid may be written as follows:

$$dm_1^\gamma = \gamma_1 y_1 p dt \quad \text{and} \quad dm_2^\gamma = \gamma_2 y_2 p dt, \quad (29)$$

where  $y_1$  and  $y_2$  are the concentrations of 1 and 2 in the vapour at pressure  $p$ , and  $\gamma_1$  and  $\gamma_2$  are known as *invasion coefficients*. Since the  $\gamma$ 's refer to the vapour phase, in which interaction between molecules is relatively small, it is assumed that  $\gamma_1$  and  $\gamma_2$  are independent of the composition of vapour and liquid. The invasion  $dm^\gamma$  is then proportional to the partial pressure of the component in the vapour phase, which is equal to  $yp$ .

If liquid and vapour are in equilibrium, no net transfer will take place, so that

$$dm = dm_1^\beta + dm_2^\beta - dm_1^\gamma - dm_2^\gamma = 0, \quad (30)$$

or, with equations (28) and (29),

$$\beta_1 x_1 + \beta_2 x_2 - \gamma_1 y_1 p - \gamma_2 y_2 p = 0. \quad (31)$$

A similar 'balance equation' must hold for each of the components separately, as the same number of molecules of each kind will enter and leave the liquid. Therefore

$$\beta_1 x_1 - \gamma_1 y_1 p = 0, \quad (32)$$

$$\beta_2 x_2 - \gamma_2 y_2 p = 0. \quad (33)$$

The last equations can be written in the form

$$\beta_1 = \gamma_1 p y_1 / x_1, \quad (34)$$

$$\beta_2 = \gamma_2 p y_2 / x_2. \quad (35)$$

We have thus expressed the  $\beta$ 's in terms of the  $\gamma$ 's, the composition of the phases and the total pressure of the vapour. But we must note that the terms entering in these equations have *equilibrium values*; that is to say, the  $\beta$ 's and  $\gamma$ 's, in this particular case, refer to the same temperature,  $p$  is the vapour pressure of the liquid at this temperature, and  $y_1$ ,  $y_2$  are the concentrations of both components of a vapour in equilibrium with a liquid of composition  $x_1$ ,  $x_2$ . To remind us of this, we shall add a bar to  $p$ ,  $y$ , and  $\gamma$  in these equations:

$$\beta_1 = \bar{\gamma}_1 \bar{p} \frac{\bar{y}_1}{x_1}, \quad (36)$$

$$\beta_2 = \bar{\gamma}_2 \bar{p} \frac{\bar{y}_2}{x_2}. \quad (37)$$

The bar indicates that those values of  $p$ ,  $y$ , and  $\gamma$  must be taken which hold for equilibrium with the liquid phase chosen.

We shall now suppose that the equilibrium of the system is disturbed. This means that the temperature of the vapour differs from that of the liquid and (or) the composition of the vapour differs from that of a vapour in equilibrium with the liquid. The result may be that liquid evaporates, or that vapour condenses, or that merely the compositions of the phases change. In general, the relative amounts and compositions of the phases will both be altered, as usually happens in a rectifying column. Rectification must therefore be considered as the general case. Bošnjaković correctly points out that there is no point in trying to draw a sharp distinction between rectification and evaporation and between rectification and condensation. In each case there will be an exchange of molecules between the phases, and the differences between the several phenomena lie merely in the net direction of flow. If many more molecules pass from the liquid to the vapour than vice versa, we speak of evaporation; if the opposite is true we call it condensation, and if the total amount of molecules moving in each direction is about the same (but not the total amount of each particular kind of molecule), we are dealing with rectification.

In the general case, the amount of the substance 1 transferred from the liquid to the vapour in the time  $dt$  through unit surface will be

$$dm_1 = dm_1^\beta - dm_1^\gamma = (\beta_1 x_1 - \gamma_1 p y_1) dt, \quad (38)$$

and for the substance 2,

$$dm_2 = dm_2^\beta - dm_2^\gamma = (\beta_2 x_2 - \gamma_2 p y_2) dt. \quad (39)$$

$p$  is here the actual pressure and need not be the same as the equilibrium vapour pressure  $\bar{p}$  of the liquid with a composition  $x_1$ ,  $x_2$ .

We can now replace  $\beta_1$  and  $\beta_2$  by their equilibrium values, as given in equations (36) and (37), so that

$$\frac{dm_1}{dt} = \bar{\gamma}_1 \bar{p} \bar{y}_1 - \gamma_1 p y_1, \quad (40)$$

$$\frac{dm_2}{dt} = \bar{\gamma}_2 \bar{p} \bar{y}_2 - \gamma_2 p y_2, \quad (41)$$

or, if we introduce partial pressures with  $p_1 = p y_1$ ,  $p_2 = p y_2$ ,

$$\frac{dm_1}{dt} = \bar{\gamma}_1 \bar{p}_1 - \gamma_1 p_1, \quad (42)$$

$$\frac{dm_2}{dt} = \bar{\gamma}_2 \bar{p}_2 - \gamma_2 p_2, \quad (43)$$

and the total amount of both components together, passing from the liquid to the vapour phase in time  $dt$ , will be

$$dm = dm_1 + dm_2, \quad (44)$$

and  $dm \geq 0$ .

With the help of the kinetic theory of gases, the following relationship may be deduced for  $\gamma$  as a function of the absolute temperature  $T$  and the molecular weight  $\mu$ :

$$\gamma = g \frac{1}{\sqrt{(\mu T)}}; \quad (45)$$

$g$  depends only on the state of motion of liquid and vapour, and is therefore the same for both components. Similarly, both components of a single phase are at the same temperature. Equations (42) and (43) may therefore be written in the form

$$\frac{dm_1}{dt} = \frac{g}{\mu_1^{\frac{1}{2}}} \left( \frac{\bar{p}_1}{T_L^{\frac{1}{2}}} - \frac{p_1}{T_G^{\frac{1}{2}}} \right), \quad (46)$$

$$\frac{dm_2}{dt} = \frac{g}{\mu_2^{\frac{1}{2}}} \left( \frac{\bar{p}_2}{T_L^{\frac{1}{2}}} - \frac{p_2}{T_G^{\frac{1}{2}}} \right), \quad (47)$$

where  $T_L$  and  $T_G$  are the temperatures of the liquid and vapour respectively, and

$$\frac{dm}{dt} = \frac{dm_1}{dt} + \frac{dm_2}{dt}.$$

For water boiling in an open vessel,  $g$  was observed to be about  $0.8 [(^{\circ} \text{ abs.})^{\frac{1}{2}}/h]$ . It is probable that  $g$  is fairly close to this value for any type of perforated rectifying plate.

These are the fundamental formulae on which all calculations of equilibration phenomena in binary two-phase mixtures may be based. In particular we may use equations (46) and (47) to compute the efficiency of a plate in a column. For if we can solve the equations for a particular case, we know  $m_1$  and  $m_2$  as a function of  $t$ . If we then determine the time during which the vapour is in contact with the liquid on the plate, we can find out how much of each component passes from one phase to the other and thus calculate the actual change of composition of the phases.

Apart from the molecular weights of the components,  $dm/dt$  depends on the temperatures of both phases separately, on the actual partial pressures in the vapour and the partial pressures that would subsist in equilibrium with the liquid on the plate. Since the partial pressure is defined as the product of total pressure and concentration, it contains

two variables in itself. Thus, equations (46) and (47) contain a large number of variables, the mutual dependence of which is difficult to determine. To obtain a figure for the efficiency of a plate, without going through very intricate calculations, we shall have to approximate rather crudely.

If we take the case of oxygen-nitrogen mixtures, the molecular weights of the components are 32 and 28 respectively. As only the square root of  $\mu$  enters into the equations, we shall not go far wrong if we put  $\mu_1 = \mu_2 = 30$ .

In the upper column of a rectifying plant, in which the pressure is 1 atm., the temperature in the condenser is  $90^\circ$  abs. and the nitrogen leaves the top of the column at about  $77.5^\circ$ . The temperature head between the top and bottom of the column is therefore  $12.5^\circ$ , or 16.2 per cent., and the square root of the temperature head, which is of interest for our equation, is 8 per cent. This corresponds to a change in composition of 100 per cent. between the top and bottom of the column. A similar relation between the changes of temperature and composition will hold for a single plate. So we can, without incurring a very considerable error, put  $T_L = T_G = \text{const.}$  for a single plate.

As regards the pressures that enter into each equation, we have no choice but to pretend that they are equal, though we know quite well that they are not. But any other assumption would complicate matters too much. It can be shown that the error incurred will not distort the results very far.

If we make all these simplifying assumptions, equation (46) boils down to the following simple form:

$$\frac{dm_1}{dt} = \frac{gp}{\sqrt{(\mu T)}} (z_1 - y_1), \quad (48)$$

in which we suppose 1 to refer to nitrogen. We assume  $g = 0.8$ ,  $p = 1$  atm., and  $\mu = 30$ .  $z_1$  is the nitrogen concentration in a vapour in equilibrium with the liquid on the plate, and  $y_1$  the actual nitrogen concentration in the vapour at the time  $t$ .

To simplify matters still further, we shall assume that the heats of evaporation of oxygen and nitrogen are the same, as we did earlier in this chapter. The effect of this is that the size of each bubble remains unchanged during its passage through the liquid. Only its composition changes, and we have what we may term a case of 'pure rectification'. Thus

$$\frac{dm_1}{dt} + \frac{dm_2}{dt} = 0. \quad (49)$$

Since the composition of the liquid is regarded as a constant with regard to time, the only variable in equation (48) is  $y_1$ , and we may write

$$\frac{dm_1}{dt} = a(z_1 - y_1) \quad (50)$$

with 
$$a = \frac{gp}{\sqrt{(\mu T)}}. \quad (51)$$

Now let  $y_0$  be the nitrogen concentration in the bubble when it enters the plate at  $t = 0$ . Let  $M$  be the constant mass of the bubble and  $S$  its surface. Then at a given time  $t > 0$ ,

$$M_1 = My_0 + Sm_1, \quad (52)$$

$$y_1 = M_1/M = y_0 + Sm_1/M, \quad (53)$$

or, if we put  $M/S = m$ ,

$$y_1 = y_0 + m_1/m. \quad (54)$$

Equation (50) then becomes

$$dm_1/dt = a(z_1 - y_0 - m_1/m). \quad (55)$$

At  $t = 0$ ,  $m_1 = 0$  and  $y_1 = y_0$ ; and at  $t = \infty$ ,  $y_1 = z_1$ . Therefore the solution of (55) is

$$m_1 = (z_1 - y_0)m(1 - e^{-at/m}). \quad (56)$$

Now  $(z_1 - y_0)m$  is the total amount of nitrogen that must enter the bubble per unit surface in order that complete equilibrium may be attained. Therefore

$$q = \frac{m_1}{m(z_1 - y_0)} \quad (57)$$

is the degree of equilibrium reached up to the time  $t$ , and we may write

$$q = 1 - e^{-at/m}. \quad (58)$$

Since  $m_1/m = y_1 - y_0$  from equation (54),

$$q = \frac{y_1 - y_0}{z_1 - y_0}. \quad (59)$$

Thus, at the moment of leaving the liquid,  $q$  is identical with the efficiency  $\epsilon$ .

If we replace the mass  $m$  per unit surface by the radius  $r$  of the bubble, which we assume to be spherical, and reduce both quantities to the same units, we finally obtain

$$\frac{a}{m} = 6.84 \sqrt{\left(\frac{T}{\mu}\right)} \frac{g}{r}, \quad (60)$$

where  $r$  is in centimetres.

We see from equation (58) that the time required to produce a certain degree of equilibration  $q$  is independent of the original composition of liquid and vapour. If the composition of the vapour was originally far removed from the equilibrium value, many molecules will be transferred in a short time; if the original composition was close to equilibrium, few molecules will be transferred. But in both cases, after a given time, the degree of equilibration  $q$  will be the same. This means that, at any rate in our approximation, the efficiency of all the plates of a column is the same.

To ascertain how far these formulæ are correct, and more especially how far the approximations were justified, we can use the results here obtained to compute the efficiency of the plates of a certain column, and then see how far the figures tally with the known efficiency of the column as a whole. We shall take the large Linde air column described in Chapter VII under (4), since the dimensions of this apparatus are well known. As we saw, the plant separates 6,800 cub. m. of air per hour. The pressure in the lower column is 5 atm., that in the upper column 1 atm. The perforation of the plates is 0.8 mm. in diameter.

By taking the mean temperature in each column and assuming  $g = 0.8$ , we obtain the following values of  $a/m$ :

lower column:  $a/m = 81$ ;

upper column:  $a/m = 77$ .

This gives us the following table for  $q$  as a function of  $t$  in seconds.  $l$  refers to the lower and  $u$  to the upper column.

TABLE 24. *Degree of Equilibration  $q$  on the Plates of a Large Linde Air Column as a Function of Time*

$t$ (sec.)	$q_l$	$q_u$
0.01	0.555	0.537
0.02	0.802	0.785
0.03	0.910	0.901
0.04	0.962	0.954
0.05	0.983	0.979
0.06	0.992	0.991

The period of time required for equilibrium to be attained within a few per cent. is thus seen to be of the order of some hundredths of a second.

We must now ascertain how long the vapour is really in contact with the liquid on the plate. From the known quantities of vapour



moving in the various parts of the column, we find that, in the space between the plates, the velocity of the vapour is

$$v_l = 5.325 \times 10^4 \text{ cm.}^3/\text{sec.},$$

$$v_u = 26.9 \times 10^4 \text{ cm.}^3/\text{sec.},$$

in the lower and upper columns respectively.

To determine the velocity of the bubbles on the plates, we must know the effective cross-sections of the vapour in the liquid. This cannot be determined accurately. For the bubbles will remain bubbles in the liquid and will only fill a portion of the cross-section of the plate itself. Since only part of the plate is perforated and we have no quantitative data as to how the bubbles spread out in the liquid, we can only make a rough guess at the effective cross-section. We shall assume, rather arbitrarily, that the effective cross-section is one-third of the total cross-section of the column. We then find for the period of time during which the vapour is in contact with the liquid,

$$t_l = 0.042 \text{ sec.},$$

$$t_u = 0.0107 \text{ sec.}$$

This gives us, with the help of Table 24,

$$\epsilon_l = 0.966,$$

$$\epsilon_u = 0.556.$$

We see that the efficiency in the lower column is practically unity, whereas it is much smaller in the upper column.

The theoretical number of plates for  $\epsilon = 1$  has been computed for this particular column by A. Weissberg.† On the other hand, we know the actual number of plates in the upper and lower columns.‡ The ratio of these figures should give us the actual efficiency of the plates. The data are collected in Table 25 and compared with the values we have just computed.

TABLE 25. *Efficiency of the Plates of a Large Linde Air Column*

	$n_t$	$n_a$	$\epsilon_a$	$\epsilon$
Lower column . .	23	24	0.96	0.966
Upper column . .	14	36	0.39	0.556

$n_t$  signifies the theoretical number of plates for  $\epsilon = 1$ , according to Weissberg's calculations;  $n_a$  is the actual number.  $\epsilon_a = n_t/n_a$  may be

† A. Weissberg, *Journal of Technical Physics* (Russian), **4**, 1204 (1934).

‡ S. Gersch, *Glubokoe Okhlazhdenie* (Low-temperature Engineering), part ii, Moscow, 1937.

called the actual efficiency of the plates,  $\epsilon$  is the efficiency we have calculated.

We see that  $\epsilon_n$  and  $\epsilon$  are of the same order of magnitude, which seems to corroborate the line taken in the calculations. The agreement in the lower column is far closer than the accuracy of the calculations justifies and must therefore be taken as somewhat fortuitous. The agreement for the upper column is probably all that we have a right to expect, but it is actually rather better than it seems. For apart from the fact that the manufacturers would tend to add a few plates in the final column, to make sure of obtaining the required purity of the products, even when deviations occur in the régime, there is another much more important reason why the efficiency must needs be smaller in this column than the calculated figure. This is connected with the fact, hitherto neglected, that air is not really a binary mixture at all. We shall see in the next chapter that the rare gases, in particular argon, play a very important role in the functioning of an air plant and greatly reduce the efficiency of the upper column.

## IX

### THE SEPARATION OF AIR (4)

#### AIR AS A TERNARY MIXTURE

##### 1. The influence of argon on the production of oxygen and nitrogen

THE composition of atmospheric air, as given in Table 1, justifies us in considering it, to a first approximation, as a binary mixture of oxygen and nitrogen. Moreover, we should expect that, as we study the separation process in greater detail, the influence of argon would next make itself felt, whereas the other rare gases, in view of their low concentrations, would only become apparent as a result of exhaustive investigation. In actual fact, as long as our aims are limited to the production of oxygen and nitrogen of a purity compatible with technical requirements, the presence of krypton and xenon in atmospheric air never becomes manifest at all, while the influence of neon and helium, though appreciable, is easily eliminated. Argon, however, which is present in a concentration of just under 1 per cent., affects the production of oxygen and nitrogen to a much greater extent than might be expected. This fact, which was ascertained by Hausen† as late as 1934, will concern us in the present section.

There are, however, two distinct attitudes which may be adopted towards the rare gases as constituents of atmospheric air. One is to consider their influence on the production of pure oxygen and nitrogen, the other to find ways and means of extracting them in a pure condition. In the first case the rare gases are considered as undesirable impurities, in the second they are themselves primary products of separation. This second question will be treated in the next section.

We may state at once that, in spite of the large number of components present in the atmosphere, their concentrations and thermal properties are such that we are never forced to bear them all in mind simultaneously. When discussing argon we are at liberty to forget the presence of other rare gases; in considering neon and helium we can neglect oxygen and argon. Only in very exceptional cases need we turn our attention to more than three components at the same time. Though these components will differ according to the particular problem treated, yet for all practical purposes we can confine ourselves to ternary mixtures.

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, 5, 290 (1934).

The presence of 0.94 per cent. of argon in the atmosphere makes it impossible to obtain pure oxygen and pure nitrogen simultaneously in the plants described in Chapter VII. The one or the other product must needs be contaminated with argon. If all the argon is collected with the oxygen, the latter cannot be more than 95 per cent. pure; on the other hand, if the argon is extracted with the nitrogen and the oxygen is pure, the purity of the nitrogen cannot exceed 98.7 per cent. Since the boiling-point of argon lies between the boiling-points of oxygen and nitrogen, we can in principle choose with which product it will emerge from the plant. In the general case both products will be more or less contaminated. In the plants discussed in Chapter VII, and which will further concern us in this section, no provision is made to dispose of the argon otherwise. The plants have two exits only and the argon must emerge through one of them.

This is the first and most obvious reason why the presence of argon cannot be neglected in the separation of oxygen and nitrogen. The second may be deduced from the following considerations. Since the boiling-point of argon lies between the boiling-points of oxygen and nitrogen, we should expect the boiling- and dew-curves of argon-oxygen mixtures and of argon-nitrogen mixtures to lie closer together than those of oxygen-nitrogen mixtures. On the other hand, we know that, the closer together the boiling-curve and dew-curve of a mixture, the more difficult that mixture is to separate, that is to say, the smaller will be the effect of each plate and therefore the more plates will be needed. We may thus conclude that on those plates of an air column on which pure oxygen and pure nitrogen are to be obtained, it is not so much oxygen and nitrogen that are being separated, but oxygen and argon or nitrogen and argon, and, in view of the proximity of the boiling- and dew-curves of these mixtures, this separation will require a considerable number of plates.

Indeed, if we compare the ( $T$ ,  $x$ ) diagrams of oxygen-nitrogen and oxygen-argon in Figs. 30 and 32, we see immediately that the equilibrium curves of the latter are very much closer than those of the former. For example, an oxygen-nitrogen liquid mixture at 1 atm. containing 80 per cent. of oxygen is in equilibrium with a vapour containing 49 per cent. oxygen, whereas a liquid mixture with 80 per cent. oxygen and 20 per cent. argon is in equilibrium with a vapour containing 71 per cent. oxygen and 29 per cent. argon. Similar differences, though less pronounced, hold good in argon-nitrogen mixtures, when compared with those of oxygen and nitrogen.

These simple considerations indicate that the presence of nearly 1 per cent. argon in atmospheric air may have a more serious effect on the production of oxygen and nitrogen than is apparent at first sight. A more detailed analysis will show that, under certain circumstances, a very considerable accumulation of argon will occur in certain parts of an air column, and that the removal of this argon from the oxygen or nitrogen product is a serious matter. It will then become clear that the apparently low efficiency of the plates in the upper Linde column, noted at the end of Chapter VIII, is, in fact, due to a low effect, resulting from the preponderance of argon on certain plates.

To make this clear we must see what theory can contribute to an understanding of the separation of ternary mixtures.

All quantitative data regarding rectification must be based on the equilibrium diagram of the system under discussion. In the case of oxygen–nitrogen–argon, the full equilibrium diagram of the ternary system has not yet been determined experimentally. Referring back to Chapter II, we see that the three binary systems have been studied fairly accurately. For  $O_2$ – $N_2$  we have the classical work of Dodge and Dunbar, for  $A$ – $N_2$  the work of Holst and Hamburger, and for  $A$ – $O_2$  preliminary measurements of Inglis and a more recent and detailed paper by Bourbo and Ischkin. Before the latter work appeared, Hausen† constructed an equilibrium diagram of the ternary system on the basis of existing experimental results, coupled with theoretical considerations involving an integration of the Duhem-Margules equation. Hausen represented the results of his calculations in the form of a triangular diagram with two superimposed systems of coordinates, as described in Chapter II and shown in Fig. 16. Though the accuracy may not be of a very high order, we have no reason to doubt the general trend of the diagram, which is probably accurate enough for practical purposes.

Hausen developed his theory of the separation of ternary mixtures not so much with a view to calculating the number of plates required as in order to obtain an insight into the increase and decrease of the concentrations of the several components as the mixture moves along the column. His theory does not therefore aim at determining the compositions in steps from one plate to the next, but develops continuous smooth curves giving the composition of the mixture. This is equivalent to assuming a very low efficiency of the plates or, which comes to the same thing, a packed column with no plates at all. The

† H. Hausen, *Forschung auf dem Gebiet des Ingenieurwesens*, 6, 9 (1935).

smooth curves so obtained can be broken up later into discontinuous steps if required.

Consider a portion of a rectifying column containing a ternary mixture, which we shall suppose to be oxygen, nitrogen, and argon. In a certain section let  $x_o$  and  $x_a$  be the oxygen and argon concentrations in the liquid, and  $y_o$  and  $y_a$  the concentrations in the vapour.  $z_o$  and  $z_a$  are the equilibrium vapour concentrations corresponding to a liquid of the composition  $x_o$  and  $x_a$ . The nitrogen concentrations  $x_n$ ,  $y_n$ , and  $z_n$  are determined by the fact that the three  $x$ 's,  $y$ 's, and  $z$ 's must add up to unity. Let  $M_l$  be the amount of liquid and  $M_g$  the amount of vapour flowing past a given section in a given time. As in the case of oxygen-nitrogen mixtures, we may assume as a first approximation that the heats of evaporation of the three components are the same. It can then be proved as before that  $M_l$  and  $M_g$  are constant throughout the column. In considering the balance equations of a portion of the column, we can then neglect the balance of heat and only take the balance of mass and composition into account. Then, if  $\bar{x}_o$ ,  $\bar{x}_a$ ;  $\bar{y}_o$ ,  $\bar{y}_a$  are the given concentrations of liquid and vapour on a certain section, the concentrations  $x_o$ ,  $x_a$ ;  $y_o$ ,  $y_a$  on any other section will be given by the equations

$$\left. \begin{aligned} M_l x_o - M_g y_o &= M_l \bar{x}_o - M_g \bar{y}_o, \\ M_l x_a - M_g y_a &= M_l \bar{x}_a - M_g \bar{y}_a, \end{aligned} \right\} \quad (1)$$

which may be written

$$\left. \begin{aligned} y_o &= \bar{y}_o - \frac{M_l}{M_g} \bar{x}_o + \frac{M_l}{M_g} x_o, \\ y_a &= \bar{y}_a - \frac{M_l}{M_g} \bar{x}_a + \frac{M_l}{M_g} x_a. \end{aligned} \right\} \quad (2)$$

Now suppose the column to contain plates of the 'old-fashioned' type, on each of which the liquid is homogeneous. It can be proved that the efficiency  $\epsilon$  of a plate is the same for each component. Then the change of composition undergone by a vapour on passing through a plate will be

$$\left. \begin{aligned} \Delta y_o &= \epsilon(z_o - y_o), \\ \Delta y_a &= \epsilon(z_a - y_a), \end{aligned} \right\} \quad (3)$$

so that

$$\frac{\Delta y_o}{\Delta y_a} = \frac{z_o - y_o}{z_a - y_a} \quad (4)$$

irrespective of  $\epsilon$ . This equation will also hold when  $\epsilon \ll 1$ .

Now consider the diagram in Fig. 125, in which oxygen concentrations are measured along the base and argon concentrations along the left side. Let  $\bar{L}$  and  $\bar{G}$  be two points with the concentrations  $\bar{x}_o$ ,  $\bar{x}_a$

and  $\bar{y}_o$ ,  $\bar{y}_a$  at a certain section of the column. Then, as we proceed along the column, the points  $L$  and  $G$ , representing the composition of liquid and gas on various sections, will describe curves. If the changes in composition on each plate are sufficiently small, these curves will be approximately smooth.

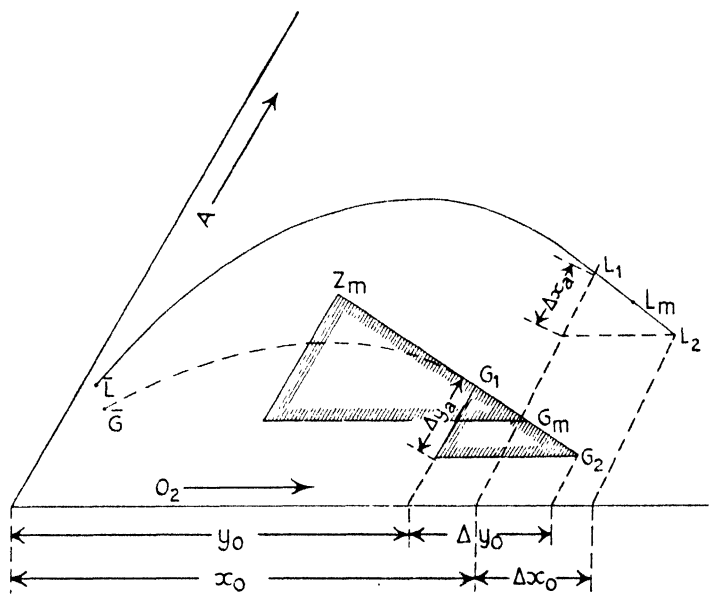


FIG. 125. Graphical method for determining rectification curves of ternary mixtures

Suppose  $\Delta y_o$  and  $\Delta y_a$  to signify changes in composition of the gas extending over a number of very small steps. Then the  $y$ 's and  $z$ 's in (4) must be replaced by mean values, so that

$$\frac{\Delta y_o}{\Delta y_a} = \frac{z_{om} - y_{om}}{z_{am} - y_{am}}. \quad (5)$$

Suppose the curves have already been determined from the points  $\bar{L}$  and  $\bar{G}$  to  $L_1$  and  $G_1$  with the coordinates  $x_o$ ,  $x_a$  and  $y_o$ ,  $y_a$  respectively, and we wish to determine their further course. We can first choose arbitrarily an increment  $\Delta x_o$ . Then, according to (2),  $\Delta y_o$  will be given as  $\Delta y_o = \Delta x_o M_l/M_g$ . We now extrapolate the liquid curve to where we believe the middle of this step to be, reaching a point  $L_m$  with the coordinates  $x_{om}$ ,  $x_{am}$ . The vapour in contact with this liquid will be represented by a point  $G_m$  with the coordinates  $y_{om}$ ,  $y_{am}$ . Let the point  $Z_m$  with the coordinates  $z_{om}$ ,  $z_{am}$  represent a vapour in equilibrium with  $L_m$ . If we now join  $Z_m G_1$ , the projection of this straight line will pass

through  $G_m$  and thus also through the required point  $G_2$  with the coordinates  $y_o + \Delta y_o$  and  $y_a + \Delta y_a$ . This is proved from the fact that, in the shaded triangles, which are similar, equation (5) is fulfilled. Since, according to (2),

$$\Delta y_a / \Delta y_o = \Delta x_a / \Delta x_o, \quad (6)$$

the increment  $L_1 L_2$  of the liquid curve must be laid parallel to that of the vapour curve and should pass through the extrapolated point  $L_m$ , which it usually does. If it does not, the construction must be repeated and  $L_m$  more judiciously chosen.

The lines for the liquid and vapour obtained in this way are known as *rectification curves*. As may be seen from equations (2), they depend on the concentrations  $x_o, x_a; y_o, y_a$  and the ratio  $M_l/M_g$ .

Let us now apply this method to the practical case of atmospheric air. We shall first consider a single column of the type described in Chapter VII, p. 158, No. 1, and lay down as a condition that we wish to obtain pure oxygen in the evaporator.

If  $\bar{x}_o, \bar{x}_a$  and  $\bar{y}_o, \bar{y}_a$  are the compositions of liquid and vapour at the top of the single column, and  $x_o, x_a; y_o, y_a$  the composition in the evaporator, we have

$$\begin{aligned} \bar{x}_o &= 20.9, & x_o &= y_o = 100, \\ \bar{x}_a &= 0.93, & x_a &= y_a = 0. \end{aligned}$$

$\bar{y}_o$  can be chosen arbitrarily within certain limits, but it can in no case be smaller than 6.15 per cent., which would be the oxygen concentration of a vapour in equilibrium with liquid air.

Equations (2), referring to the top and bottom of the column, may now be written as follows:

$$\left. \begin{aligned} y_o &= \bar{y}_o - \frac{M_l}{M_g}(\bar{x}_o - x_o), \\ y_a &= \bar{y}_a - \frac{M_l}{M_g}(\bar{x}_a - x_a). \end{aligned} \right\} \quad (7)$$

Since  $\bar{x}_o, x_o$ , and  $y_o$  are given, a choice of  $\bar{y}_o > 6.15$  per cent. determines  $M_l/M_g$  according to (7). Since  $\bar{x}_a, x_a$ , and  $y_a$  are given,  $\bar{y}_a$  is also determined. For  $\bar{y}_o = 6.15$  per cent.,  $\bar{y}_a$  becomes 1.1 per cent.

In Fig. 126 the rectification curves are shown, as computed by Hausen with the construction given above, for various values of  $\bar{y}_o$  ranging from 6.15 to 8 per cent., and the values of  $M_l/M_g$  deduced from the first part of (7). The full curves represent the liquid phase, the dotted lines are for the vapour. These curves are very remarkable and



merit detailed attention. They show the change in composition of the liquid and gaseous mixtures on their way down the column.

The first fact that strikes us is that the curves end along the argon-oxygen axis. Thus, as we expected, the final stages of the process consist in rectifying an argon-oxygen mixture, the nitrogen having been completely displaced by the argon.

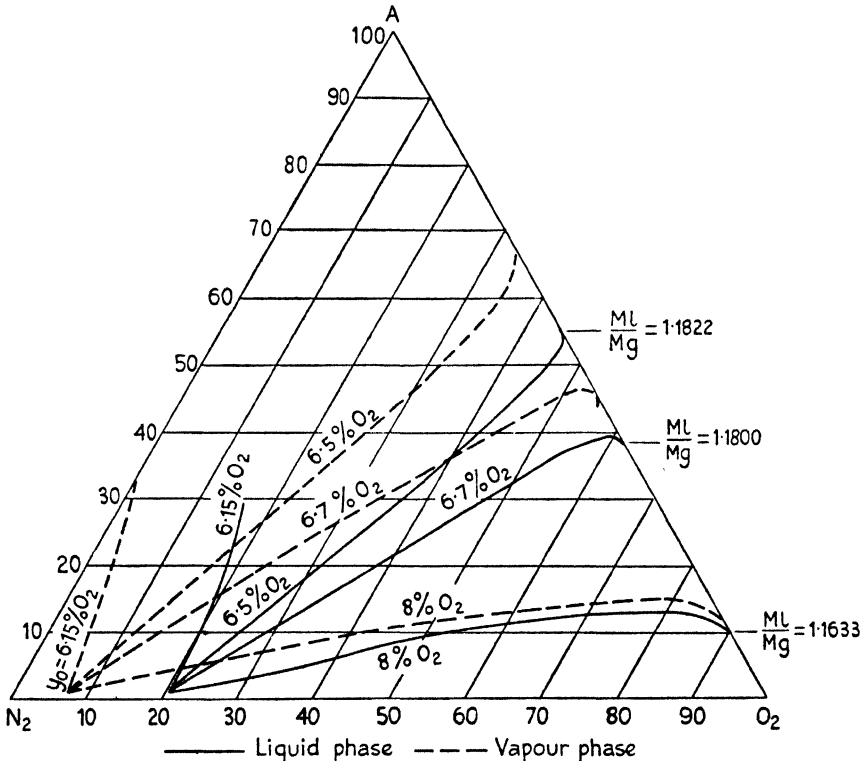


FIG. 126. Theoretical rectification curves in a single column for different oxygen contents of the nitrogen product

Secondly, even in the lowest curve, for  $\bar{y}_o = 8$  per cent.  $O_2$ , a very considerable argon accumulation occurs in the column. From 0.93 per cent. at the top, the argon concentration rises to about 12 per cent. in the liquid and 15 per cent. in the vapour, before it finally decreases to zero at the bottom of the column.

If we choose  $\bar{y}_o = 6.7$  per cent., this effect is still more marked. The argon concentration rises to 39 per cent. in the liquid and 45 per cent. in the vapour. Finally, the curves bend down sharply and continue along the argon-oxygen axis.

If  $\bar{y}_o$  is lowered to 6.5 per cent., the plant ceases to function. The curves bend round in the opposite direction and end at 84 per cent. argon in equilibrium with its vapour instead of pure oxygen. That is to say, we should obtain rich argon at the bottom of the column if we were in a position to maintain the ratio  $M_l/M_g = 1.1822$ . We cannot do this, as we have not enough argon to remove at the bottom of the column. The curves for  $\bar{y}_o = 6.5$  per cent., and 6.15 per cent. have therefore no physical significance. Between the curves for  $\bar{y}_o = 6.5$  per cent. and 6.7 per cent. we could find one rectification curve to intersect the oxygen–argon axis without bending round at all. It has been shown that such lines exist for all values of  $\bar{x}_o$ ,  $\bar{x}_a$  and that they are almost straight. Hausen calls them *demarcation lines*, as they mark the limits up to which the column will work. Every point on the argon–oxygen axis marks the end of one and only one demarcation line.

We see further that the argon accumulation increases with increasing values of  $M_l/M_g$ , i.e. the more oxygen is removed from the base of the column.

In order to show the detrimental influence which the accumulation of argon in the column exerts on the effect of the plates, we can plot the ‘distance from equilibrium’  $y_o - z_o$ , expressed in oxygen concentration, in any cross-section of the column, as a function of the oxygen concentration of the vapour. This has been done in Fig. 127 for oxygen concentrations of emerging vapour of 6.7 and 8 per cent., and for hypothetical ‘air’ containing no argon at all, as treated in the last chapter. It is evident that  $y_o - z_o$  is very much smaller in the presence of argon, especially in the lower part of the column. The points at which the curves begin to bend downwards correspond to the cross-sections of the column at which the argon accumulation is at its greatest. Below these points rectification takes place mainly between oxygen and argon, since the rectification curves in Fig. 126 are almost indistinguishable from the argon–oxygen side of the triangle. The small values of  $y_o - z_o$  are therefore due to the proximity of the boiling- and

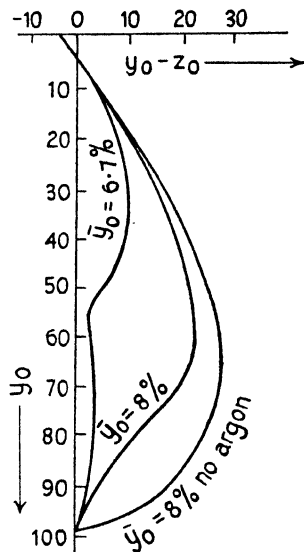


FIG. 127. ‘Distance from equilibrium’ in respect of oxygen in a single column as a function of the oxygen content of the vapour for different oxygen contents of the nitrogen product and for air free of argon

dew-curves in the equilibrium diagram of the argon-oxygen system. They will require more plates than are needed in the case of a binary oxygen-nitrogen mixture.

Similar considerations hold good in a double column. But here we must treat the influence of the argon on the nitrogen as well as on the oxygen. Besides the demarcation lines that end on the argon-oxygen

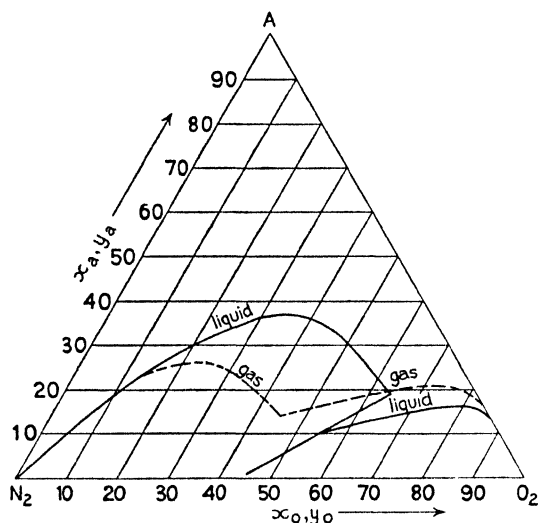


FIG. 128. Theoretical rectification curves in the upper part of a double air column

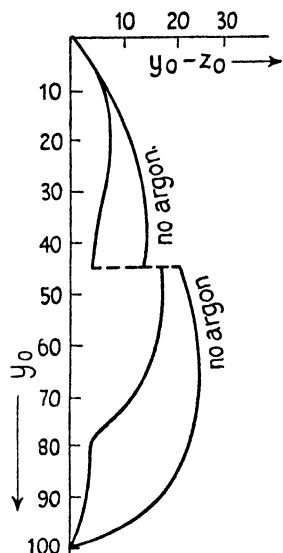


FIG. 129. 'Distance from equilibrium' in respect of oxygen in the upper part of a double air column as a function of the oxygen content of the vapour for the case represented in Fig. 128 and for air free of argon

side of the triangle, we shall have another series of such lines ending on the argon-nitrogen side. The lower column may be treated in the same way as a single-column plant, except that now nitrogen and not oxygen is the component to be purified. A typical liquid and vapour rectification curve for the upper column is shown in Fig. 128, in which it is assumed that the mixture  $M$  entering in the middle is completely liquid and contains 45 per cent.  $O_2$  and 1.7 per cent.  $A$ . The curves on the left are for the part of the column above the inlet, those on the right are for the lower part of the upper column.

Finally, Fig. 129 shows  $y_o - z_o$  in the upper column as a function of the oxygen concentration  $y_o$  in the vapour, and the corresponding

values for a mixture of oxygen and nitrogen without argon. It is clear that the reduced effect of the plates in the lower part of the upper column will appear as a low efficiency in the calculations carried out at the end of the last chapter.

## 2. The production of argon

We now come to the problem of producing argon from atmospheric air. In the following we shall consider argon, not as an unwelcome admixture, hindering the production of oxygen and nitrogen, but as a primary product in itself. Argon is used in large quantities for filling incandescent lamps, as its high molecular weight hinders the evaporation of the filaments. In this respect it is a great improvement on the old nitrogen filling. An important condition is that the argon shall be completely free from oxygen. Small admixtures of nitrogen are innocuous and even desirable, since pure argon is liable to produce luminous discharges which give a coloured light and ruin the lamp.†

It is almost impossible to produce argon from the air without at the same time producing oxygen and, to a lesser degree, nitrogen in a state of fairly high purity. Nor would it be economical to do so. For since air contains less than 1 per cent. of argon, large quantities of air have to be treated for every cubic foot of argon extracted. This entails a high consumption of power, which would render the argon too expensive for practical purposes if the same power did not simultaneously produce oxygen. All argon plants are therefore at the same time oxygen plants.

In extracting argon from the air we come up against the problem of separating a ternary mixture into its components. Clearly the plants discussed in Chapter VII are insufficient to serve this purpose, and some innovation will be required.

In principle, a ternary mixture, consisting of the three components *A*, *B*, and *C* (arranged in order of rising boiling-points), can be separated into its components with the help of two columns or sets of columns as follows. The mixture is first separated into pure *A* and a mixture of *B* and *C*, and in a second column pure *B* and pure *C* are extracted. Or else *B* may first be extracted with *A*, pure *C* emerging from the first column, after which *A* and *B* can be separated in the second column. In the case of argon, the boiling-point of which is closer to that of oxygen than to that of nitrogen, the first arrangement appears the most obvious. However, owing to its low initial concentration, there would still be so little argon in the second column that a very

† About a thousand million incandescent lamps are filled with argon every year.

strong reflux would be required to raise the concentration sufficiently, and this would lead to a high power consumption.

It is more profitable to make use of the accumulation of argon in the first column, as demonstrated in the last section, and to withdraw an *argon fraction* from a section of the column at which the argon concentration is sufficiently high and, at the same time, the nitrogen concentration sufficiently low. A rich argon mixture is then obtained at the top of the second column and pure oxygen at the bottom of both columns.

To bring about separation in the argon column, the latter must be equipped with an evaporator and a condenser, i.e. heat must be continually supplied to the base of the column and withdrawn from the summit. Since the argon fraction enters the column as a liquid and both products leave it as vapours, the heat balance appears to be fairly well assured. The agent for supplying heat to the evaporator and withdrawing it from the condenser is usually taken from the primary air column, though it may be supplemented by an auxiliary cycle.

An argon column coupled with a Linde double air-separating plant, a combination applied in most argon works, is shown in Fig. 130. The argon fraction leaves the upper air column at about 1.4 atm. abs. from a plate *A*, at which the argon concentration is fairly high and the nitrogen concentration almost negligible. It is introduced at *P* in the middle of the argon column. Gaseous nitrogen at about 5.5 atm. abs. is withdrawn at *B* from the condenser of the lower air column, condensed in the evaporator at the bottom of the argon column at *N*, reduced to 1 atm., and admitted at *L* to the condenser, where it is evaporated, condensing argon in the tubes around which it boils. Finally, it leaves the column at *H*. Almost pure oxygen is withdrawn from the evaporator at *E* and a gas rich in argon leaves the condenser at *D*. Both products and the evaporated nitrogen are passed through heat-exchangers and leave the plant at room-temperature and atmospheric pressure.

In practice, the argon fraction leaving the primary air column contains between 7 and 12 per cent. argon and rather less than 1 per cent. nitrogen. The oxygen product of the argon column contains hardly a trace of nitrogen and about 0.2 per cent. argon. In the cycle here described, the gas leaving the top of the argon column contains about 60 per cent.  $A$ , 35 per cent.  $O_2$ , and 5 per cent.  $N_2$ . The oxygen is usually removed chemically by means of hydrogen or sulphur, and the final product consists of about 92 per cent.  $A$  and 8 per cent.  $N_2$ . This

so-called *technical argon* is employed directly for filling incandescent lamps.

The calculations for the primary air column, in which the argon content must, of course, be taken into account, can be carried out according to the lines laid down by Hausen, as described in the last section, or according to a method described by Fischer.† This will not concern us here and we shall consider the argon column only. Even so the problem contains so many possible variables that a complete discussion would go beyond the scope of this book, and we shall therefore neglect the nitrogen in the argon column and treat the process as the separation of a binary mixture. As in Chapter VI, we shall consider the process on the ( $h$ ,  $x$ ) plane.

Let  $m_A$  and  $h_A$  be the mass and specific enthalpy of a 'phase'  $A$  and let  $x_A$  be its composition in per cent. argon by weight. We shall fix once and for all two variables of the system, which refer to products of the primary air column.

1. The composition of the liquid argon fraction is 11 per cent.  $A$  and 89 per cent.  $O_2$ . ( $x_P = 11$  per cent. by weight.)

2. For every pound of air entering the primary column, 0.25 lb. of pure gaseous nitrogen is diverted to serve as a refrigerant in the argon column.

It will be noted that  $m_P$ , the amount of argon fraction per pound of air, has not been fixed. It will depend on the 'argon yield' of the primary column, i.e. on how much argon is lost with the oxygen and nitrogen products. Altogether there is 0.013 lb. of argon in every pound of air. If the argon yield of the primary column were 100 per

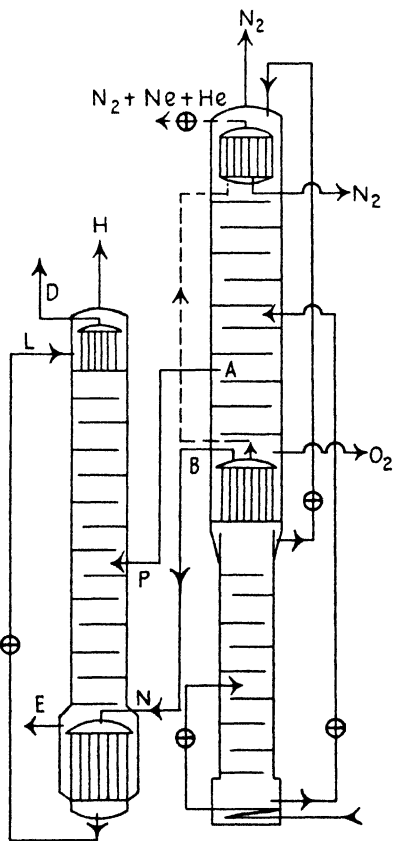


FIG. 130. Argon column combined with Linde double air column

† V. Fischer, *Zeitschrift des Vereins Deutscher Ingenieure*. Beiheft 'Verfahrenstechnik', No. 3, p. 87 (1938).

cent.,  $m_P$  would be  $0.013 \times 100/11 = 0.118$ . In practice  $m_P$  is usually not much more than half this value. 0.25 lb. of nitrogen per pound of air is the maximum quantity of refrigerant available, without destroying the régime of the primary column.

The following table contains the 'fundamental points' of the argon column with the values of those variables that have been fixed *a priori*:

Point	$m$	$x$	$h$
$P$	..	11	5
$D$	..	..	..
$E$	..	0	50.4
$N$	0.25	$N_2$	56
$L$	0.25	$N_2$	14.7
$H$	0.25	$N_2$	53

In the table the oxygen leaving the argon column is taken as pure, as the fraction of a per cent. of argon it contains would have little influence on the subsequent discussion. The values of  $h$  are in calories per gramme and taken from existing diagrams.  $h_p$  is not very accurate.

Of the remaining four variables ( $h_p$  depends only on  $x_D$  and is therefore not counted as a variable) two may be chosen arbitrarily between certain limits, whereupon the rest are automatically fixed, as we shall now show.

The balance equation of the column as a whole reads

$$P + q = D + E + H - N, \quad (8)$$

where  $q$  is the heat loss through the lagging. This may be written

$$P + q = D + E - Q_1 + Q_2, \quad (9)$$

where  $Q_1$  is the heat introduced into the evaporator and  $Q_2$  the heat withdrawn from the condenser.

For the balance of weight and composition we thus have

$$m_P = m_D + m_E, \quad (10)$$

$$m_P x_P = m_D x_D + m_E x_E. \quad (11)$$

Substituting (10) in (11), we obtain

$$m_D = m_E \frac{x_P - x_E}{x_D - x_P}. \quad (12)$$

Thus, if we introduce the values already fixed and choose  $m_E$  and  $x_D$ ,  $m_D$  may be determined from (12) and  $m_P$  from (10). For the argon yield we then have

$$\alpha = m_D x_D / 0.013. \quad (13)$$

For example, if we put  $m_E = 0.05$  and  $x_D = 60$  per cent., we obtain

$$m_D = 0.05 \times 11 / (60 - 11) = 0.011,$$

$$m_P = 0.05 + 0.011 = 0.061.$$

This gives  $\alpha = 0.011 \times 60 / 0.013 = 51$  per cent.

In fixing the values of the free variables, we must consider that a high yield of argon is profitable as well as a high argon concentration in the final product. Unfortunately these two conditions are irreconcilable. For, as equation (12) shows, a large value of  $x_D$  entails a small value of  $m_D$ , and this more than counterbalances  $x_D$  in equation (13). From (12) it is, however, clear that we can increase  $x_D$  without lowering  $m_D$  or  $\alpha$ , if we simultaneously increase  $m_E$ . But there is a definite limit above which  $m_E$  cannot be raised, as the following argument shows.

Fig. 131 represents a rough ( $h, x$ ) diagram of argon-oxygen mixtures at atmospheric pressure, obtained by putting the enthalpies of saturated liquid oxygen and argon equal to zero and neglecting the heats of mixing in both phases. In this case the liquid boundary line coincides with the axis of abscissae, and the vapour curve is a straight line joining two points on the ordinate axes that mark off the heats of evaporation  $\lambda_o$  and  $\lambda_a$  of oxygen and argon respectively. The former is 50.4 cal. per gm., the latter 38.0 cal. per gm. The connodals are taken from the equilibrium curves, as determined by Bourbo and Ischkin.

The liquid argon fraction, containing 11 per cent. A, is expanded from 1.4 to 1.0 atm. abs. before it enters the column. This causes some liquid to evaporate and reduces the argon content of the liquid to about 9 per cent., which, when the column is properly adjusted, is equal to the argon concentration on the first plate below the entry. Point  $P'$  in Fig. 131 gives the position of this liquid on the boundary line.

Now, as was proved in Chapter IV, there is a point  $Z$  on the ( $h, x$ ) diagram such that  $L-G=Z$ , if  $L$  and  $G$  denote liquid and gas in contact on any horizontal section of the column below the point of entry, and the number of plates required in this part of the column is obtained by joining the liquid ends of the connodals to  $Z$  and producing to the vapour curve. Moreover, it was shown that the column will not function unless the straight line  $P'Z$  is steeper than the connodal through  $P'$ .  $Z'$ , where the projection of the connodal through  $P'$  cuts the oxygen axis, is therefore the highest value that  $Z$  can have when



pure oxygen is to be obtained. We find  $h_{Z'} = -82$  cal. per gm. Now the balance equation of the lower part of the column reads

$$L - G = E - Q_1 = Z, \quad (14)$$

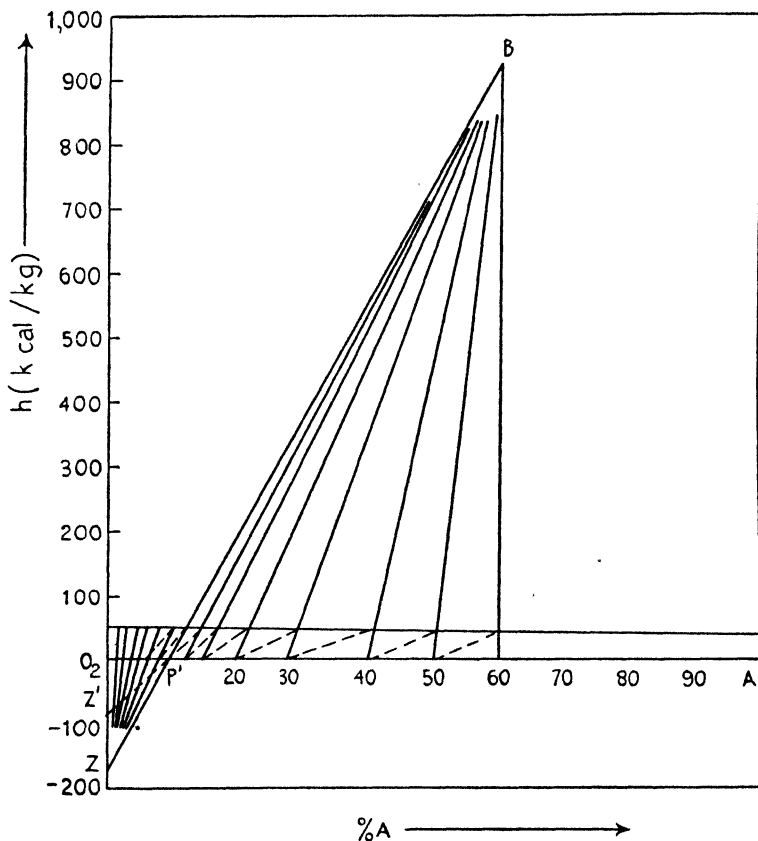


FIG. 131. Graphical determination of the number of plates required in an argon column on the  $(h, x)$  diagram of oxygen-argon mixtures

which means

$$h_Z = h_E - Q_1/m_E, \quad (15)$$

$$Q_1 = m_N \lambda_{N_2},$$

where  $\lambda_{N_2}$  is the latent heat of evaporation of nitrogen at 5.5 atm. and is equal to 41.3 cal. per gm. Since  $m_N = 0.25$ , we have

$$Q_1 = 0.25 \times 41.3 = 10.3 \text{ cal.}$$

With  $h_E = 50.4$  cal., equation (15) gives

$$h_Z = 50.4 - 10.3/m_E. \quad (16)$$

From the above it is apparent that only those values of  $m_E$  are permissible for which  $h_Z \leq -82$  cal. This gives

$$m_E \leq 0.078 \text{ gm.}$$

It should be noted that this limiting value is independent of  $x_D$  and depends only on  $x_P$ . Thus  $m_E = 0.078$  gives us the maximum yield for any value of  $x_D$ .

With the help of equations (10), (12), and (13) we obtain the following values of  $\alpha$  for various values of  $x_D$  and  $m_E$ .  $x_P$  is always taken as 11 per cent. and  $m_N = 0.25$  cal.

TABLE 26. *Argon Yield  $\alpha$  in per cent. as a Function of Argon Concentration of Product  $x_D$  and Amount of Oxygen  $m_E$  emitted at Base of Column*

$x_D \backslash m_E$	0.05	0.06	0.07	0.078
50	56	67	78	87
60	51	61	71	79
70	50	60	70	78
80	49	59	69	77
90	48	58	68	75

Though an increase of  $m_E$  within permissible limits considerably raises the argon yield without lowering the concentration of the product, it has the disagreeable effect of increasing the number of plates required for rectification. From Fig. 131 it is clear that  $m_E = 0.078$ , which leads to  $h_Z = -82$ , entails an infinite number of plates in the argon column. The values in the last column of Table 26 are therefore fictitious. But even values of  $m_E$  in the vicinity of 0.078 lead to a large number of plates, in view of the proximity of liquid and vapour curves on the equilibrium diagram of oxygen and argon.

For  $m_E = 0.05$  and  $x_D = 60$  per cent., Fischer showed that fifteen plates are theoretically sufficient if we allow 0.5 per cent. A in the oxygen product ( $x_E = 0.5$ ). Assuming a plate efficiency of about 70 per cent., we should need twenty-two plates in practice. Fig. 131 shows how the number of plates was determined.

If we turn once again to equation (9) we can compute  $Q_2$  from  $h_H$  and  $h_L$  and find  $Q_2 = 9.6$  cal. Since  $Q_1 = 10.3$  cal., we see that more heat is supplied to the evaporator than is withdrawn from the condenser. So the nitrogen in the argon column does not act as a refrigerant in the ordinary sense of the word, except in so far as it maintains the temperature head between top and bottom of the column. Taken as

a whole, it supplies more heat than it withdraws. This was to be expected, for since the argon fraction is introduced as a liquid, and the products are removed as vapours, it is heat and not cold that is needed to maintain the process.

If we insert the known values of the terms in (9), we find for the heat losses, which are now the only unknown,

$$q = 2 \text{ kcal. per kg. of air.}$$

For small plants this is plausible, and here the heat leakage, together with  $Q_1 - Q_2$ , is sufficient to evaporate the oxygen. But in large aggregates, where the argon column is heavily lagged and close to a large, cold air column, the heat leakage is usually smaller. In this case a certain amount of compressed air from the primary column is passed through a separate coil in the evaporator and ensures a sufficient evaporation of the oxygen.

The Linde air-argon aggregate is not the only type of plant used to produce argon, but it is probably the type most widely applied. Several modifications exist, one being the addition of a separate auxiliary nitrogen cycle to increase the argon yield. In other types of plant the argon column is placed inside the air column. This is very good for purposes of heat insulation, but has the disadvantage of making the inner column inaccessible. On the whole it has been found profitable to increase the argon yield at the expense of purity, though the subsequent disposal of the surplus oxygen is rather expensive. Subsidiary units have also been devised to obtain very pure argon from the rich mixtures that form the product of the column here described.

### 3. Neon and helium

When a double air column works for long periods at a stretch it is generally found that the efficiency of the condenser-evaporator begins to fall off. The impression made is that the heat transfer between condensing vapour in the tubes and evaporating liquid around them deteriorates. This is due to the formation of an uncondensable cushion of gas, first in the dome above the condenser and finally in the tubes of the condenser itself. This gas is mainly nitrogen, but the gradual accumulation of neon and helium has so far lowered the partial pressure of the nitrogen that the existing pressure and temperature are insufficient to condense it rapidly enough. This effect is enhanced by the insufficiently rapid diffusion of neon and helium away from the walls of the tubes, where it becomes concentrated owing to the condensation of nitrogen.

This disturbing influence of neon and helium, which are themselves uncondensable under the operating conditions, is easily eliminated by blowing off the contents of the condenser at intervals through an exhaust tube attached to the top of the dome. Thus the effect of neon and helium on the production of oxygen and nitrogen is much less pronounced than that of argon. This is due partly to the low concentration of these gases in atmospheric air (see Table 1) and partly to the fact that their boiling-points are much lower than those of both oxygen and nitrogen and not, as that of argon, between the two. Yet since the condenser is normally closed at the top, all the neon and helium passing through the plant, except for the very small traces that dissolve in the liquid nitrogen, must accumulate in the condenser and gradually fill it, if it is not removed.

The brilliant red light emitted by neon discharge tubes has created a demand for the gas in recent years, mainly for advertising purposes. Some air separators are therefore fitted out with auxiliary equipment for extracting a neon-helium fraction instead of merely blowing it off to the atmosphere.

The gas collecting in the condenser has a very low concentration of neon and helium, at any rate if it is blown off frequently enough to secure the proper functioning of the air column. But a simple device enables the neon and helium to be concentrated. The pressure in the condenser tubes is about 5 atm. and the temperature about 93° K., whereas the temperature at the top of the upper column is 78° K. If we introduce a small additional condenser at the top of the column and pass a small current of gas from the dome of the main condenser through it at 5 atm. pressure (see Fig. 130), a considerable portion of the nitrogen in this gas will condense and the neon-helium fraction will become richer. The composition of the final neon-helium fraction varies somewhat, but the average figures are roughly as follows:

TABLE 27. *Composition of Neon-Helium Fraction,*  
*per cent. by volume*

N <sub>2</sub>	.	.	.	70 per cent.
Ne	.	.	.	23 "
He	.	.	.	7 "

The nitrogen can easily be removed by compressing the mixture to some 50 atm. and passing through a dephlegmator surrounded by liquid air or liquid nitrogen. The remaining traces of nitrogen can be adsorbed on charcoal at liquid air temperature, or, if this entails too great a loss of neon, absorbed on hot calcium or magnesium. It is important to

remove all nitrogen from the mixture, as its presence destroys the colour and brilliancy of the discharge. On the other hand, helium has very little effect on the discharge, and 'technical neon', containing about 30 per cent. He is frequently employed in discharge tubes.

The separation of neon from helium is difficult and expensive, since neither can be condensed at temperatures attainable with liquid air or liquid nitrogen, the stock refrigerants of the low-temperature engineer. The lowest temperature attainable with liquid nitrogen is the triple point,  $63^{\circ}\text{K.}$ , at which the vapour pressure is 9 cm. of mercury, a pressure difficult to maintain in a technical plant. But the critical temperature of neon is  $42^{\circ}\text{K.}$  and that of helium  $5.2^{\circ}\text{K.}$  To separate neon and helium, we must either employ a refrigerant colder than nitrogen or have recourse to other methods.

Theoretically, the most economic way to separate these gases would be to pass a compressed neon-helium mixture through a condenser cooled with liquid neon. The neon could be liquefied with the help of liquid air in a plant of the Linde type. But at present pure neon is not available in sufficiently large quantities to be used as a refrigerant, and the unavoidable losses in compressors and pipe-lines would be prohibitive.

Meissner† succeeded in separating some thousand cubic feet of neon-helium mixture with the help of liquid hydrogen, in order to obtain helium for laboratory purposes. His plant, which was on a semi-technical scale, was built at the Physikalisch-technische Reichsanstalt at Charlottenburg. The laboratory had a large plant for producing about 12 litres of liquid hydrogen per hour by the Linde method, and this plant was so well constructed that only 1 litre of liquid nitrogen was needed for each litre of liquid hydrogen produced. Liquid hydrogen was therefore a comparatively cheap refrigerant. The neon-helium mixture, slightly above atmospheric pressure, was passed through a condenser cooled with liquid hydrogen. The neon was thus condensed, and the helium, with very small admixtures of neon, remained in the gaseous state. The remnants of neon were removed with active charcoal.

The boiling-point of hydrogen is  $20.4^{\circ}\text{K.}$  and that of neon  $27.2^{\circ}\text{K.}$  There is thus no difficulty in condensing the neon in liquid hydrogen. However, the triple point of neon lies at  $24.6^{\circ}\text{K.}$ , above the boiling-point of hydrogen. Precautions have therefore to be taken to prevent the

† W. Meissner and K. Steiner, *Zeitschr. f. d. gesamte Kälteindustrie*, **39**, 49 and 75 (1932).

neon from solidifying and blocking the tubes. This difficulty can be eliminated by maintaining the pressure above the liquid hydrogen at 3 atm., which suffices to raise its boiling-point above the triple point of neon. Another possibility is to raise the temperature head between the condensing neon and the evaporating hydrogen by artificially reducing the heat transfer. Both these methods have been applied successfully.

Small quantities of neon and helium may be separated very effectively by fractional sorption on charcoal at low pressures and liquid-air temperatures. An elegant method for doing this has recently been developed by Glückauf. By a suitable arrangement of sorption tubes and mercury cut-offs a complete separation can be effected in a couple of hours.

From the industrial point of view, the separation of neon and helium is of interest only for producing neon. Helium obtained from air is far too expensive to compete with the cheap helium produced from natural gas, as will be described in Chapter XI. It is only at those times and places at which helium from natural gas is unobtainable that it may be worth while extracting helium from air by separating it from neon. But even then this has never been done on a large scale. Meissner's experiments were carried out in Germany after 1918, when no helium could be obtained from America, even for experimental purposes.

#### 4. Krypton and xenon

Since the boiling-points of the heavy rare gases, krypton and xenon, are higher than those of all the other constituents of atmospheric air, these substances will naturally tend to accumulate in those parts of separating plant that show the highest oxygen concentrations. Since oxygen is easily removed by chemical means, small quantities of mixtures may be obtained, consisting mainly of argon and nitrogen, but containing quite appreciable traces of krypton and xenon. By a series of arduous small-scale processes the heavy rare gases can then be separated from the other components and ultimately from each other.

This laboratory technique was fairly satisfactory as long as krypton and xenon were required only for scientific experiments. But it became hopelessly inadequate as soon as large quantities of these gases were required for industrial purposes.

The issue was raised on a completely new level when it was suggested that krypton and xenon could advantageously replace argon for the filling of incandescent bulbs. Their high atomic weight reduced

vaporization of the filaments very considerably, allowing higher temperatures to be used in the lamp with a corresponding increase in efficiency, and their low thermal conductivity made it possible to reduce the size of the bulbs.

At about the same time it was shown that krypton is a very useful gas for filling discharge lamps, as the light it emits, if suitably blended with other vapours, produces an effect similar to daylight.

In recent years much work has been done, especially in France, but also in Hungary and other countries, on the utilization of krypton and xenon in lamps and their separation from atmospheric air.

The most obvious scheme appeared to be the production of krypton and xenon as by-products of air separation. By introducing subsidiary equipment in existing separating plant, it seemed possible to obtain krypton and xenon or a mixture of the two without much additional expense in plant and power consumption. For industrial purposes a separation of the two is unnecessary, and we can assume that xenon will always appear together with krypton. We shall therefore refer to krypton only in future.

However, these hopes were soon shown to be illusory mainly owing to the very low concentration of krypton in the air. In every cubic metre of air there is only 1 cubic centimetre of krypton and 0.1 c.c. of xenon. To fill one thousand million incandescent lamps, the number now annually filled with argon, about 1,000,000 cub. ft. of krypton would be required. Assuming that the krypton yield from air were 100 per cent., this would require  $10^{12}$  cub. ft. of air to be treated, which is more than the consumption figure of all the air-separating plant of the world. Thus, if every oxygen plant and every nitrogen plant were fitted out with additional krypton units, they would not produce sufficient krypton to satisfy the world requirements.

But, quite apart from this, it was found that additional units in existing separating plant gave a very low krypton yield, and in recent years, at the suggestion of Claude, research has been carried on mainly with a view to devising a new type of plant designed for the special purpose of producing krypton.

The difficulties of this are very clear. There is 10,000 times less krypton than argon in the air, and yet we are asked to produce krypton at a price not very much higher than that of argon. The cost of the gas for filling incandescent bulbs can be only a fraction of the cost of the lamp itself, and the additional cost of replacing argon with krypton is to be smaller than the economy obtained by using less glass and

burning the lamps at a higher temperature. At the time of writing, the krypton lamp has emerged from vague speculation into the realm of undoubted possibility. Whether or not it will survive and oust the argon lamp from its dominant position is as yet undecided.

Of course, the difficulty of separating a constituent from a mixture depends not only on its initial concentration but on a number of other factors as well. The production of krypton is facilitated by the fact that its boiling-point is higher than those of both oxygen and nitrogen. If it lay between the two, as in the case of argon, separation would be exceedingly difficult. On the other hand, certain difficulties occur which were not at first expected. Owing to the low concentration of krypton and hence the large quantities of air that must be treated, the fundamental problem to be solved is that of power consumption. In all separating plant, power is consumed by compression, and the compression of vast quantities of air, at least a million cubic feet for every cubic foot of krypton produced, is exceedingly costly. It is thus essential to work at low pressures, in spite of the fact that this entails voluminous plant. Moreover, the purification of large volumes of air, especially at low pressures, is no easy matter. The absorption of water vapour and carbon dioxide consumes a large amount of caustic soda and other chemicals. From previous discussions it is clear that here is the place for cold accumulators instead of ordinary heat-exchangers. For accumulators purify the gas without the use of chemicals and are specially advantageous at low pressures. The plant developed by Claude does indeed employ such accumulators.

Ordinary air-separating plant requires about 4 atm. pressure in the main cycle and an auxiliary high-pressure cycle for about 10 per cent. of the air circulated. The 4 atm. are essential to enable all the air to be liquefied in the course of the cycle, after which it is again evaporated. All rectifying plants contain this as an important feature. But it would be far too expensive to compress all the air to 4 atm., not to mention the high-pressure cycle itself. A process was therefore sought which did not require the liquefaction of all the air in the course of the cycle, but which would enable the krypton to be extracted from the air without liquefying more than a small portion of it. The problem was solved by the Air Liquide Co. by the development of a new type of scrubbing process.

The essential feature of this process is that a large quantity of gaseous air is scrubbed in counter-current by a small quantity of liquid air, as a result of which almost all the krypton is removed from the gas and



dissolved in the liquid. The krypton content of the large quantity of gas is thus transferred to the small quantity of liquid, giving a rich krypton mixture, which is further enriched in the plant by partial evaporation and rectification. In this way it is possible to remove almost all the krypton from air at a pressure of only 1.7 atm. abs., only about 5 per cent. being compressed further to 15 atm.

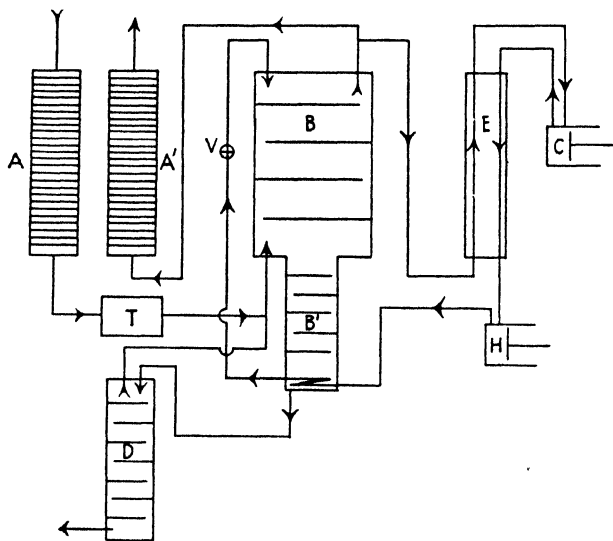


FIG. 132. Krypton plant of the Air Liquide Co.

The plant envisaged in Claude's original patent† (1933-5) is sketched in Fig. 132. The air, compressed to 1.7 atm. abs. and not previously purified, is cooled in one of the alternating cold accumulators *A*, *A'* and expanded in the turbine *T*, which it leaves as a saturated vapour at  $-190^{\circ}\text{C}$ . It is then admitted at the bottom of the upper portion *B* of a rectifying column, where it is scrubbed with a small quantity of liquid air, from which the krypton has already been removed. This scrubbing liquid is obtained by withdrawing a small portion of the air at the top of the column, warming it up to room-temperature in the heat-exchanger *E*, and compressing it to 15 atm. in the compressor *C*. The compressed air is thereupon cooled again in *E* and expanded to 2 atm. in the expansion engine *H*. It is then liquefied in the evaporator at the bottom of the lower column *B'*, expanded to atmospheric pressure in the throttle valve *V*, and delivered at the summit of *B*. After traversing *B*, the liquid, which now holds all the krypton formerly

† British Patent 432,644.

contained in the much larger quantity of air, is further enriched in the lower column *B'*. The unevaporated liquid residue is delivered from the evaporator of *B'* to the summit of the subsidiary column *D*, in which the krypton concentration is raised further. The final purification from *D* is effected by other methods, which will be discussed later.

In a subsequent patent† (1936-7) the Air Liquide Co. developed the scrubbing process so as to combine it with nitrogen production, thus returning to a certain extent to the original idea of producing krypton as a by-product of the air-separating industry. But the alteration in existing air plant, as here suggested, is very much more radical than would have been deemed necessary a few years earlier, and it would be more accurate to regard this new process as a way of making air separation a subsidiary process of the krypton industry.

The krypton scrubbing process may be combined with any of the standard methods of air separation. Fig. 133 shows how it can be used in conjunction with the two-column rectifying plant. The upper column *B*, working at atmospheric pressure, has a wide section *B'*, fitted with a small number of the usual plates. A quantity of atmospheric air, which can be twenty times as great as the amount separated in the column, is admitted at *I* at the bottom of *B'*, scrubbed with liquid nitrogen and liquid air taken from the lower column *A*, and withdrawn at *K*, after giving up all its krypton to the liquid. A liquid fraction, containing most of the krypton, is removed at *L* at the bottom of *B*, and fairly pure oxygen vapour, containing some of the krypton, is withdrawn at *F*. One or both of these fractions can be further treated for krypton. The air to be separated in the two columns is introduced as usual at the bottom of the lower column *A* at a pressure of some 4 atm. As the reflux in *B* is sufficient to produce more nitrogen than it contains itself, the amount of air withdrawn at *K* can be smaller than that admitted at *I*. The production of krypton is thus combined

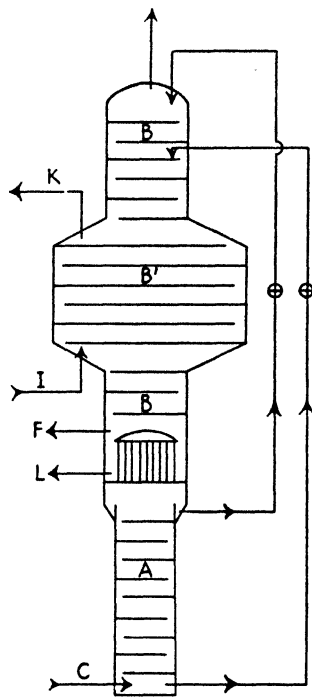


FIG. 133. Double column for krypton and nitrogen

† British Patent 468,872.

with an increased production of nitrogen in the air column. A similar process can be conducted in a single-column nitrogen plant and in a nitrogen dephlegmator of the original Claude type.

The Vereinigte Glühlampen und Elektrizitäts-Aktiengesellschaft at Ujpest in Hungary has been working on similar lines to the Air Liquide Co., and has also developed the krypton scrubbing process.† In their 1935-6 patents the importance is stressed of scrubbing the air with as cold a mixture as possible, in order to achieve a high yield of krypton. For the extraction of krypton depends to a very great extent on its vapour pressure at the scrubbing temperature. The vapour pressure of pure krypton at 90° K. is 90 mm., while at 80° K. it is only 4 mm. It is thus very much more profitable to scrub the air at 80° than at 90°. The Hungarian observers point out that the inadequacy of former methods of scrubbing was due to the fact that the air was scrubbed with liquid oxygen, boiling at atmospheric pressure and thus having a temperature of 90° K. The efficiency can be greatly increased if the air is scrubbed with liquid air, as is effected in Claude's plant and in their own apparatus, since the temperature of boiling air is about 80° K. They maintain that the krypton content of ordinary liquid air can be increased by a factor of 150 on the first plate if it is made to scrub a quantity of gas fifty times as great as itself. On the second plate, where the temperature is already higher as a result of the greater oxygen content, the increase in krypton content is a hundredfold and the efficiency drops from plate to plate on account of the rising temperature.

Several variations of the scrubbing process have been suggested, but the essential principle remains, in which the entire krypton content of a large quantity of gaseous air is extracted and concentrated in a small quantity of liquid at as low a pressure and as low a temperature as possible.

The scrubbing process, in some form or other, is an adequate method for removing krypton and xenon from atmospheric air and concentrating it in a small quantity of liquid air or oxygen. Herewith the problem of what may be called the initial concentration of krypton can be considered as solved. However, this is only half the work, and we have yet to produce from this concentrated fraction a pure mixture of krypton and xenon.

There is very little information as regards the concentration of krypton in the fractions obtained in these processes. Very probably

† British Patents 434,193; 434,194.

it is well under 1 per cent., the principal constituents being oxygen and argon. It is exceedingly difficult to obtain higher concentrations of krypton by rectification. The reasons for this are still somewhat obscure, but it is possibly connected with the low solubility of krypton in liquid oxygen. The triple point of pure krypton is  $116^{\circ}\text{K.}$ , that of oxygen  $54^{\circ}\text{K.}$  The solid-liquid equilibrium has not yet been studied, but it may well be that a precipitate is formed at low temperatures which prevents further concentration of krypton. If this is the case, it could probably be circumvented by increasing the pressure. As matters stand, the production of a pure krypton-xenon mixture is still a problem.

The oxygen can be removed easily enough by chemical means. The subsequent separation of krypton and xenon from argon can be accomplished somewhat laboriously by fractional desorption from charcoal or silica gel. Peters and Weyl† have shown that this is more effective than fractional adsorption. The whole gas is sorbed on charcoal at about  $90^{\circ}\text{K.}$ , the amount of charcoal chosen being sufficiently great to produce a very low adsorption pressure, preferably below 0.01 mm. of mercury. The temperature of the charcoal is then raised slightly and the argon pumped off with a strong diffusion pump. If the temperature is maintained sufficiently low, almost all the argon can be removed without losing much krypton. After this has been done, the charcoal is heated and krypton and xenon are desorbed without much impurity. A separation of krypton from xenon can also be achieved in this way, if desired, or the krypton-xenon mixture may be rectified. But for industrial purposes this is seldom necessary. Several other methods of concentrating krypton have been attempted, but this part of the process still seems rather unsatisfactory.

A further difficulty arises from the fact that small quantities of hydrocarbons present in the air tend to collect in the krypton fractions. Dissolved in almost pure oxygen, these substances constitute highly inflammable mixtures, and great care must be taken to avoid explosions. Several patents have been taken out, suggesting various methods of meeting this danger.

The details of krypton production are still well-guarded secrets of certain firms and it is apparent that much important work has been and is being done that is not yet available to the scientific public.

† K. Peters and K. Weyl, *Zeits. f. phys. Chemie* (A), **148**, 1 (1930).

## THE SEPARATION OF COKE-OVEN GAS

**1. Separation by partial condensation**

COKE-OVEN gas is one of the principal sources of industrial hydrogen. Though more hydrogen is produced from water gas than from coke-oven gas, the relative amount obtained from coke-oven gas is steadily increasing. At the present state of industrial development, hydrogen from coke-oven gas is rather more expensive than hydrogen from water gas, but much cheaper than electrolytic hydrogen. The separation of water gas is effected by chemical means, the carbon monoxide being converted to carbon dioxide and then absorbed. A low-temperature method invented by Frank and Cario is now obsolete. We shall therefore not discuss the production of hydrogen from water gas.

The methods evolved for separating coke-oven gas by partial condensation and rectification at low temperatures, though by no means completely satisfactory, have been developed to a considerable degree of perfection, and have given rise to standard plants designed on a very large scale. The units constructed in Germany and the U.S.S.R. separate some 200,000 cub. ft. of gas per hour. It is on the basis of experience gained with these plants that the modern apparatus is being built for the extraction of olefines from cracker gas and the by-products of the hydrogenation industry.

The aim of coke-oven gas separation is to produce hydrogen. For hydrogenation purposes the hydrogen should be as pure as possible; for the synthesis of ammonia a mixture is required containing 75 per cent. by volume  $H_2$  and 25 per cent.  $N_2$ . Adulteration with nitrogen is therefore not only permissible but even desirable. On the other hand, the catalysts on which the ammonia synthesis is effected are poisoned by very small traces of carbon monoxide or oxygen. It is therefore important that neither of these gases should be present in the final product. Since the boiling-points of nitrogen and carbon monoxide are only  $6^\circ$  apart, it is difficult to separate a product containing  $N_2$  but no CO. In effect, if the hydrogen is to be used for ammonia synthesis, the separation of coke-oven gas reduces in the main to the separation of nitrogen and carbon monoxide. In practice the other constituents of coke-oven gas, such as methane and ethylene, are not produced in anything like a pure state, but emerge in the form of several fractions, each containing two or more constituents. These fractions are often

subsequently reunited and form a gas of high calorific value, usually known as rich gas.

The problem of separating coke-oven gas differs very considerably from that of separating air for the following reasons:

1. Whereas air is essentially a mixture of two components with comparatively slight impurities, coke-oven gas, as is shown in Table 3, p. 3, contains at least six constituents with concentrations over 1 per cent.
2. Apart from the constituents listed in Table 3, crude coke-oven gas contains a number of other components, which are usually removed before the gas enters the low-temperature unit. These are not only water and carbon dioxide, which occur in air also, but considerable quantities of naphthalene, benzene, toluene, and xylene, and ammonia and several sulphur compounds. These constituents require special treatment.
3. Whereas the boiling-points of nitrogen and oxygen, the principal constituents of atmospheric air, are only  $13^{\circ}$  apart, and the condensation of one is impossible without the other, about half the coke-oven gas consists of hydrogen, which is still in the gaseous state when all the other constituents are already liquid. Since hydrogen is the principal product, rectification is in this case unnecessary and the whole process can be based on partial condensation. We shall, however, see later that, in one of the plants employed, rectification plays a certain part in the removal of carbon monoxide from the nitrogen.

The separation of a binary mixture by partial condensation was illustrated in Chapter III for the case of nitrogen and helium. It was shown that these two gases may be separated very effectively by this method. Now coke-oven gas, as we have seen, is not even approximately a binary mixture; nevertheless, some important points can be made clear by considering a binary model, consisting of the two principal components of coke-oven gas: hydrogen and methane. Following an example given by Hausen,<sup>†</sup> we shall consider a mixture, consisting of 70 per cent.  $H_2$  and 30 per cent.  $CH_4$  at 8 atm. pressure, which is to be separated by partial condensation. To simplify matters still further, we shall assume that no hydrogen dissolves in liquid methane. This is not strictly true, as may be seen from Fig. 40 on p. 51, but that is immaterial for the points we are discussing.

<sup>†</sup> H. Hausen, *Geschichte der Gesellschaft für Linde's Eismaschinen*, Wiesbaden, 1929, p. 155.

As in our example in Chapter III, methane will begin to condense at a temperature at which the pressure of its saturated vapour  $\pi_c$  is equal to the partial pressure  $p_c$  of methane in the mixture. As the total pressure  $p$  is 8 atm., and the methane concentration is 30 per cent., the partial pressure of methane before condensation commences is 2.4 atm. This is the vapour pressure of pure methane at  $-150^\circ\text{C}$ . But only a drop of methane will condense at this temperature; for as soon as condensation begins, the partial pressure of methane in the gas will drop below 2.4 atm., and the temperature will have to be lowered further in order that condensation may continue.

Let  $m_c$  be the number of moles of methane in the original mixture and  $m - m_c$  the number of moles of hydrogen, and at a given temperature suppose that  $m_l$  moles of methane have condensed. Then, if we assume that the gas laws are valid in the vapour,

$$\frac{m_c - m_l}{m - m_c} = \frac{p_c}{p - p_c},$$

whence 
$$m_l = m_c - \frac{p_c(m - m_c)}{p - p_c},$$

or, since  $p_c = \pi_c$ , 
$$m_l = m_c - \frac{\pi_c}{p - \pi_c} (m - m_c).$$

If 1 mole of gas was present to begin with, we have

$$m_l = 0.3 - \frac{0.7\pi_c}{8 - \pi_c}.$$

Knowing the vapour pressure of methane as a function of temperature, we can thus calculate the amount of methane condensed as the temperature is lowered.

The result of this calculation is shown in Fig. 134. We see that the curve giving  $m_l$  as a function of  $T$  rises steeply at first as the temperature falls, but becomes gradually flatter. At  $-161^\circ$ , the boiling-point of methane at atmospheric pressure, about 0.18 moles, or 60 per cent., of the methane has been condensed. But even at  $-180^\circ$  only 0.285 moles, or 95 per cent., is liquid. Five per cent. of the methane is still in the vapour phase, which now contains 98 per cent.  $\text{H}_2$  and 2 per cent.  $\text{CH}_4$ . Evidently hydrogen and methane can be separated quite efficiently by this method, but we must cool to very low temperatures in order to bring about anything like a complete separation. Condensation of methane takes place along a very great interval of temperature.

But this is only one of the facts which this example brings home to

us. Another concerns the refrigeration that we must supply to carry out the process. As long as the gases are merely being cooled, the heat that must be withdrawn from them for each degree through which their temperature is lowered is equal to their heat capacity. The specific heat of hydrogen at constant pressure in this temperature interval is about 7 cal./mole; that of methane about 10 cal./mole. The total heat

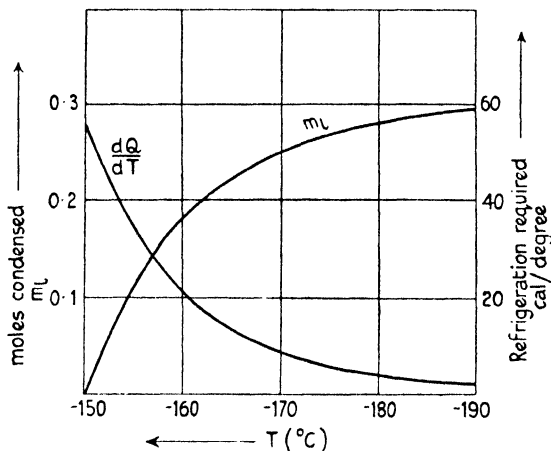


FIG. 134. Condensation of methane from a mixture containing 70 per cent.  $H_2$  and 30 per cent.  $CH_4$  at 8 atm.

capacity of the mixture is therefore about 8 cal./mole. The refrigeration needed to withdraw this heat is usually supplied by allowing a colder gas to exchange heat with the gas that is being cooled. But as soon as liquefaction sets in, latent heat of condensation must be withdrawn, and a current of cold gas seldom has a sufficient heat capacity to absorb this heat. A pure gas, or a mixture of two gases with boiling-points close to one another, condenses at a certain temperature or in a narrow temperature interval, and the heat of condensation can be absorbed by causing a second liquid to evaporate. This liquid may be either the same substance that is condensing, at a slightly different temperature and pressure, or another substance altogether. We have seen examples of this in the condensers and evaporators of air columns. But in the case of our hydrogen-methane mixture, the latent heat to be withdrawn is spread out over a long range of temperature. It is therefore much more difficult to find a suitable refrigerant.

Let us consider this problem from the quantitative side. We shall call the latent heat of evaporation of methane  $\lambda$  (cal./mole) and assume, as is approximately the case, that  $\lambda$  is independent of whether or not



the vapour is mixed with hydrogen. Then for each infinitesimal amount  $dm_i$  of methane condensed, an amount  $dQ$  of heat must be withdrawn such that

$$dQ = \lambda dm_i.$$

If  $dm_i$  is condensed by lowering the temperature by  $-dT$ , we have

$$dQ = -\lambda \frac{dm_i}{dT} dT.$$

But

$$m_i = m_c - \frac{\pi_c}{p - \pi_c} (m - m_c).$$

Therefore

$$dQ = (m - m_c) \lambda \frac{d}{dT} \left( \frac{\pi_c}{p - \pi_c} \right) dT,$$

or

$$dQ = \frac{(m - m_c) \lambda p}{(p - \pi_c)^2} \frac{d\pi_c}{dT} dT = \frac{(m - m_c) \lambda \pi_c p}{(p - \pi_c)^2} \frac{d \log \pi_c}{dT} dT.$$

But according to the Clausius-Clapeyron equation, when the vapour is a perfect gas and its volume great compared with that of the liquid,

$$\frac{d \log \pi_c}{dT} = \frac{\lambda}{RT^2},$$

and we may write

$$dQ = \frac{(m - m_c) \lambda^2 p \pi_c}{(p - \pi_c)^2 RT^2} dT.$$

In our example  $m - m_c = 0.7$  and  $p = 8$  atm. The latent heat of methane is  $\lambda = 2,000$  cal./mole, and  $R$  may be taken as 2 cal./mole deg. So we obtain

$$\begin{aligned} dQ/dT &= \frac{0.7 \times 4 \times 10^6 \times 8 \times \pi_c}{(8 - \pi_c)^2 \times 2 \times T^2} \\ &= \frac{11.2 \times 10^6 \times \pi_c}{(8 - \pi_c)^2 \times T^2}. \end{aligned}$$

Again using the known vapour-pressure curve of methane, we can now calculate  $dQ/dT$  as a function of  $T$ . In this way we obtain the second curve in Fig. 134, which shows us how much heat must be withdrawn from the hydrogen-methane mixture, over and above that needed to cool the gas, for each degree through which it is cooled during condensation. We see that this amount of heat is great at first, where condensation is rapid, and that it falls off at lower temperatures when most of the methane is condensed. The total area covered by the curve,

$\int_{-150} (dQ/dT) dT$ , must, of course, equal  $0.3\lambda$  or 667 cal. The upper limit of the integral should, strictly speaking, be the absolute zero of temperature; practically it will suffice to integrate up to about  $-200^\circ\text{C}$ .

We see that, between  $-150$  and  $-170^\circ$ , the latent heat to be with-

drawn is greater, initially indeed much greater, than the heat capacity of the gas, although  $\lambda$  is spread out over a large temperature interval. Moreover, this heat varies very sharply with the temperature. Clearly it would be difficult to use a current of gas as a refrigerant to absorb this heat.

We are therefore faced with the necessity of using a boiling liquid to absorb the heat of condensation of the vapour, even when the latter, as in our example, condenses over a wide temperature interval, and it is customary to use a pure liquid as the refrigerant, the temperature of which remains constant during evaporation. Since the refrigerant must, of course, be colder than the substance which is being cooled, the boiling-point of the refrigerant must be lower than the lowest temperature needed to condense the methane. In our example, if less than 2 per cent. of the methane is to remain, the temperature of the refrigerant must be not higher than  $-190^{\circ}$ , since a temperature head of at least  $4^{\circ}$  must be allowed to ensure a sufficiently rapid heat exchange. The only refrigerant available at this temperature is liquid nitrogen, which boils at  $-196^{\circ}$  C. at atmospheric pressure. To separate a mixture of hydrogen and methane it is thus necessary to use liquid nitrogen as a refrigerant, a substance whose normal boiling-point is very much lower than that of the methane itself.

This result can be generalized as follows. To separate a mixture of two substances with widely different boiling-points by almost complete condensation of one of the components, the mixture must be cooled well below the boiling-point of that component with the help of a liquid refrigerant whose boiling-point is lower than that of the component to be extracted.

This necessity is fraught with two very serious disadvantages. Firstly, according to Trouton's rule, the heat of evaporation of a substance is the greater the higher its boiling-point. Therefore, to condense a substance by evaporating a refrigerant of a lower boiling-point, we need more of that refrigerant than the amount of substance actually condensed. For example, the heat of evaporation of methane is 2,000 cal./mole, that of nitrogen only 1,336 cal./mole. In order to condense 1 mole of methane we must therefore evaporate 1.5 moles of nitrogen, even assuming that the heat withdrawn from the hydrogen is completely regained.

Moreover, by using liquid nitrogen to condense methane from a mixture, we must bring the nitrogen, boiling at  $-196^{\circ}$ , into contact with the mixture at a very much higher temperature—in the example

just quoted  $-150^{\circ}\text{C}$ . We thus obtain an unnecessarily large temperature head of  $46^{\circ}\text{C}$ . between the ingoing mixture and the refrigerant. Except in so far as heat exchange is accelerated, this temperature head is wasted, since it leads to an increase in entropy of the system as a whole, without any work being done by the system, and the process becomes highly irreversible. This wasted entropy  $\Delta S$ , as we saw in Chapter IV, necessitates the expenditure of an additional amount of work  $T'\Delta S$ , where  $T'$  is room-temperature, over and above the work that would be needed if the process were reversible. This additional 'irreversible work' appears as additional work of compressing the nitrogen to a higher pressure than would be necessary in a reversible process.

We see that, even in the simple case of separating a hydrogen-methane mixture, partial condensation gives rise to serious complications. These become much more marked in the case of a complex system like coke-oven gas, which consists of many components of different boiling-points. As the temperature of such a mixture is gradually lowered, one component after another begins to condense, usually dragging with it portions of other components which are partially soluble in it. The temperature intervals in which condensation occurs will vary in extent and in position with the concentrations of the components and with the pressure of the mixture. At the same time, the heat to be withdrawn in a given interval of temperature will vary quite irregularly. In one interval, where a certain component is extracted, it may be very large, in the next interval it may be small, and in the next large again. If we were to plot as a function of temperature the enthalpy of the mixture at the particular temperature, we should obtain an irregular curve with peaks and valleys, and if we want to cover these refrigeration requirements as economically as possible, we must employ our refrigerants in such a way as to provide the necessary cold but maintain the temperature of the refrigerant closely below that of the mixture being separated. The curve showing the enthalpy of all our refrigerants together should therefore follow as closely as possible the curve representing the enthalpy of the mixture.

In practice it is usually impossible to achieve a very striking similarity between the two curves. All we can really do is to achieve a balance of heat, while the temperature heads between mixture and refrigerants will be large at one point and small at another. Very much depends on the skill of the designer and on the amount of data available, which is as yet by no means complete.

## 2. The Linde-Bronn process

The considerations of the preceding section lead naturally to a process for separating coke-oven gas, based on partial condensation and on the utilization of liquid nitrogen. The Linde-Bronn process, first applied in 1924, was devised with the object of producing a stoichiometric mixture for ammonia synthesis, containing 75 per cent.  $H_2$  and 25 per cent.  $N_2$ . Great care is taken to remove all other constituents from the mixture, especially CO and  $O_2$ , but no attempt is made to obtain any other components in a state of purity. On the contrary, methane, ethylene, carbon monoxide, and considerable quantities of nitrogen leave the apparatus together in the form of 'rich gas'. As in all methods for separating industrial gases, the preliminary purification of the crude gas, before it enters the low-temperature unit, is complicated and voluminous. We shall first consider the gas as it leaves the purifying plant, free from moisture and carbon dioxide and containing no components with higher boiling-points than propylene.

The Linde-Bronn process was evolved by men who were experts in air separation according to the Linde methods. It has therefore preserved several features of the Linde air-separating plant, which forms a part of it, including the extensive use of ammonia refrigeration.

The most important element in the Linde-Bronn process is the use made of nitrogen. In these plants nitrogen is employed for three distinct ends. Firstly, it supplies all the refrigeration required at temperatures below those obtainable with ammonia; secondly, it is used to scrub out the last traces of carbon monoxide from the final product, and thirdly, it is introduced into that product to bring about the correct stoichiometric composition for the synthesis of ammonia.

A large ammonia cycle usually serves to precool the air entering the nitrogen plant as well as the coke-oven gas entering the low-temperature unit. The ammonia is made to boil under reduced pressure at  $-48^\circ C.$ , and both the nitrogen and the coke-oven gas enter the final separating plant at  $-45^\circ C.$  The coke-oven gas is maintained throughout at a pressure of about 13 atm. and the final product emerges at this pressure.

The low-temperature plant (Fig. 135) consists of a number of condensers and heat-exchangers embedded in lagging material within a single outer covering. The coke-oven gas first traverses three heat-exchangers, in which it is cooled by outgoing products. In the first,  $E_1$ , its temperature is lowered to  $-100^\circ C.$  and very little condensation

takes place. Small quantities of liquid propylene and ethane with traces of dissolved ethylene collect in the sump of the exchanger and are blown off at intervals through a valve. In the second exchanger,  $E_2$ , which the gas traverses from below, a temperature of  $-145^\circ$  is

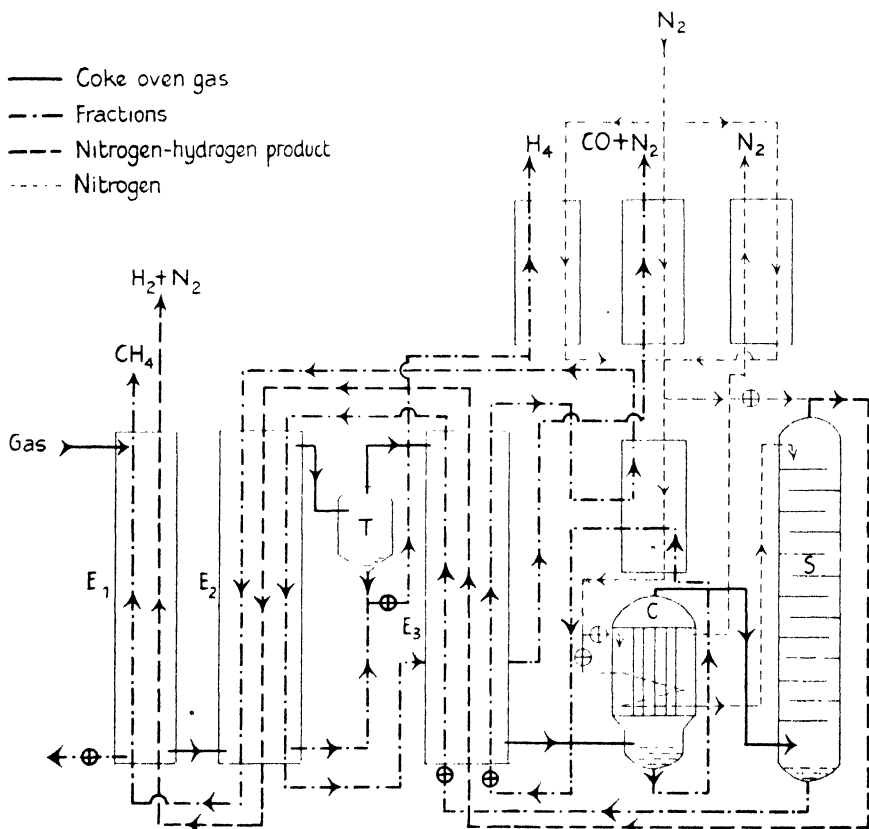


FIG. 135. The Linde-Bronn process for separating coke-oven gas

attained, sufficiently low to condense the greater part of the ethylene, the remains of the ethane and propylene, and a little methane. As the total amount of liquid formed is relatively small, the cold gaseous products are all the refrigerant required. The liquid, which is called the *ethylene fraction*, collects partly in the sump of the exchanger, the rest being carried on by the gas and deposited in a trap,  $T$ . The gas thereupon passes through the third heat-exchanger,  $E_3$ , in which it is further cooled, more methane condensing. The temperature behind this exchanger is usually given as  $-180^\circ \text{C}$ . The refrigerants in the third exchanger are methane and a mixture of nitrogen and carbon monoxide.

But, as we saw in the last section, liquid methane is not sufficiently cold to remove all the methane from the mixture. It must be supplemented by liquid nitrogen. The coke-oven gas, together with the liquid formed in the third exchanger, passes up through the tubes of a condenser *C* surrounded by liquid nitrogen boiling under atmospheric pressure. It is here cooled to about  $-190^{\circ}\text{C}$ . and almost all the methane is condensed, together with the rest of the ethylene, some oxygen, carbon monoxide, and nitrogen, and an appreciable quantity of dissolved hydrogen. The liquid, which is called the *methane fraction*, is passed into the third heat-exchanger after part of it has been evaporated in precooling the nitrogen.

The portion of the coke-oven gas which remains uncondensed in the liquid nitrogen consists of hydrogen, nitrogen, and carbon monoxide, with only traces of oxygen and methane. It must now be treated in such a way that only hydrogen and nitrogen remain. This is achieved by scrubbing it with liquid nitrogen in a long plate column *S*. The gas enters the column from below and the liquid nitrogen is introduced at the top. A liquid fraction is formed at the base of the column, consisting mainly of carbon monoxide and nitrogen. It also contains all the methane and oxygen residue that was left over from the methane condenser. The additional nitrogen, required to bring the composition up to the right proportion, is added to the product as it leaves the plate column.

The following tables show the amounts and compositions of the various fractions and gaseous mixtures as obtained in a German plant under typical conditions. The rich gas is obtained by mixing all three fractions and the gas regenerated from the purification plant.

TABLE 28. *Composition of Coke-oven Gas in the Stages of the Linde-Bronn Process*

<i>Crude Gas</i>			<i>Purified Gas</i>		
	% by vol.	cub. m.		% by vol.	cub. m.
H <sub>2</sub>	46.5	780	H <sub>2</sub>	49.3	755
CH <sub>4</sub>	26.2	440	CH <sub>4</sub>	26.6	407
N <sub>2</sub>	13.1	220	N <sub>2</sub>	13.7	210
CO	6.3	106	CO	6.6	101
CO <sub>2</sub>	3.2	54	CO <sub>2</sub>	..	..
C <sub>n</sub> H <sub>m</sub>	2.6	44	C <sub>n</sub> H <sub>m</sub>	1.8	27
C <sub>2</sub> H <sub>6</sub>	1.0	17	C <sub>2</sub> H <sub>6</sub>	1.0	15
O <sub>2</sub>	1.0	17	O <sub>2</sub>	1.0	15
	99.9	1,678		100	1,530

*Ethylene Fraction*

C <sub>2</sub> H <sub>4</sub>	30.6	15
C <sub>2</sub> H <sub>6</sub>	6.1	3
C <sub>2</sub> H <sub>2</sub>	30.6	15
CH <sub>4</sub>	30.6	15
CO	2.0	1
	99.9	49

*Methane Fraction*

CH <sub>4</sub>	74.4	372
C <sub>2</sub> H <sub>4</sub>	1.9	9.5
O <sub>2</sub>	1.2	6
CO	9.6	48
H <sub>2</sub>	4.2	21
N <sub>2</sub>	8.7	44
	100	500.5

*Carbon Monoxide Fraction*

	% by vol.	cub. m.
CO	18	52
O <sub>2</sub>	2	6
CH <sub>4</sub>	6.9	20
N <sub>2</sub>	73.1	212
	100	290

*Rich Gas*

	% by vol.	cub. m.
CH <sub>4</sub>	46.5	437
N <sub>2</sub>	28.3	265
CO	11.3	106
H <sub>2</sub>	4.9	46
C <sub>n</sub> H <sub>m</sub>	3.9	37
CO <sub>2</sub>	1.9	18
C <sub>2</sub> H <sub>6</sub>	1.4	13
O <sub>2</sub>	1.4	13
	99.6	935

*Product*

	% by vol.	cub. m.
H <sub>2</sub>	75	734
N <sub>2</sub>	25	245
	100	979

The final product and the three separate fractions, the latter expanded to atmospheric pressure, pass out of the plant after surrendering their cold to the incoming coke-oven gas and partly to the compressed nitrogen. The final product, the carbon monoxide fraction, and the methane fraction traverse the third and second heat-exchangers, the latter after exchanging some heat with the nitrogen. Only the methane fraction and the product return through the first heat-exchanger. The carbon monoxide and the ethylene fraction are used to precool the nitrogen.

Pure nitrogen, compressed to 180 atm., and taken from an air-separating plant, is precooled in a complicated system of heat-exchangers mainly with the help of the low-pressure nitrogen evaporating in the condenser. But, as mentioned above, the whole ethylene fraction and parts of the other two fractions are also utilized to cool the nitrogen. From different parts of this heat-exchanger system the nitrogen branches off to serve its three purposes. One portion is expanded to atmospheric pressure and, partially liquid, is introduced between the tubes of the condenser. Another part is expanded to 13 atm., completely liquefied in a coil within the condenser, and admitted at the

top of the plate column to scrub out the carbon monoxide; a third part is also expanded to 13 atm., and added to the product to bring about the required composition.

The low-temperature part here described is only one part of the aggregate for separating coke-oven gas. Apart from the air-separating plant needed to produce the nitrogen, the aggregate contains an intricate apparatus to purify the coke-oven gas before it is cooled to low temperature, and a large ammonia refrigerator. Crude coke-oven gas contains considerable quantities of benzene, toluene, and xylene, which may or may not be removed in the coking plant before the gas enters the separating unit. If they have not been withdrawn beforehand, the apparatus for their removal forms an important unit in the gas-separating plant. In some plants benzene and similar constituents are removed by absorption, but in large-scale aggregates this is impracticable, and it is customary to condense or freeze out the benzene vapour together with some of the moisture. This is achieved in a refrigerating plant using liquid ammonia. But this unit is separated from the actual low-temperature plant described above, except in so far as the same ammonia compressor serves both systems. The coke-oven gas, after passing through the benzene unit, emerges at room-temperature and must then again be cooled to  $-45^{\circ}\text{C.}$  with liquid ammonia before it proceeds farther.

In the usual type of plant the benzene unit consists of two pairs of heat-exchangers working alternately. The crude gas is first precooled to about  $+10^{\circ}\text{C.}$  in one exchanger by means of cold purified gas and then further cooled to  $-40^{\circ}$  in a second heat-exchanger, supplied with liquid ammonia boiling under reduced pressure. Benzene and similar constituents are thus deposited, mainly in the liquid state, and drained off. At the same time, water is condensed and some ice formed on the surface of the exchanger. The dry gas, freed from benzene, etc., is passed back through the first exchanger, which it leaves close to room-temperature, after precooling the incoming crude gas. After some time the two exchangers become clogged with ice and have to be warmed up. This is done by turning the current of gas into the other two heat-exchangers of the pairs mentioned above. The purified warm coke-oven gas is then passed through one of the cold heat-exchangers, which is thus warmed up again, the ice melting and draining away. At the same time the ammonia heat-exchanger is traversed by warm ammonia. In this way, by reversing the current at intervals, the plant can function for several weeks without a stoppage.



### 3. The scrubbing of ternary mixtures

With the help of considerations in this and former chapters, most of the processes occurring in the Linde-Bronn plant can be understood without further explanation, more especially the formation of one liquid fraction after another in the various heat-exchangers and the condenser. It is, however, difficult to calculate accurately the amount and composition of each fraction separately, since this not only depends on the variable composition of the crude gas, but also requires a very accurate knowledge of the equilibrium diagrams of the complicated systems of which the fractions consist. Always at least three and mostly four components are involved in a fraction, and we can form only an approximate picture of the phases formed by neglecting one or other of the components occurring in small concentrations. Our present knowledge of the binary and ternary systems occurring in coke-oven gas is rapidly supplying us with the information necessary. Thus recent investigations on the ethylene-methane system contribute considerably to our understanding of how the ethylene fraction is formed, and the work published on the  $\text{H}_2\text{-CH}_4$ ,  $\text{H}_2\text{-N}_2$ ,  $\text{N}_2\text{-CH}_4$ , and  $\text{H}_2\text{-N}_2\text{-CH}_4$ † systems enables us to work out fairly accurately the composition of the methane fraction as a function of temperature and pressure.

We have, however, come up against one new element in the Linde-Bronn process which requires some further thought; and that is the scrubbing column, in which carbon monoxide and remnants of other constituents are removed from the final product. This apparatus differs from the plate-columns we have discussed in previous chapters in that a special scrubbing liquid, which is not a part of the gas to be separated, is introduced at the top of the still.

The question arises as to whether the scrubbing process occurring in this unit is essentially the same as or different from what takes place in a rectifying column.

As we have seen, rectification is based on the differences in vapour pressure of two components of a mixture at the same temperature. These differences lead to the particular shape of the equilibrium curves and thence to the fact that a vapour and a liquid in equilibrium with one another have different compositions. Does this hold for a scrubbing process?

We can answer this question and obtain an insight into what happens in a scrubbing column‡ by considering the equilibrium curves of the

† See Chapter II.

‡ See M. Ruhemann and N. Zinn, *Phys. Zeits. d. Sowjetunion*, **12**, 389 (1937).

ternary system  $H_2-N_2-CO$ , which were shown in Fig. 38, p. 50. For our purpose it will be sufficient to take only these three components into account, since the remnants of oxygen and methane have no appreciable part to play in the process. Since their boiling-points are higher than those of the other components, they will naturally collect in the carbon monoxide fraction.

The boiling-points of nitrogen and carbon monoxide are only  $6^\circ$  apart, and throughout the column the concentration of nitrogen is everywhere higher than that of  $CO$ . The difference in temperature between the top and bottom of the plate column will therefore be small, probably less than  $2^\circ C$ . Therefore, although the small temperature heads between the plates of the column will play a considerable part in the exchange process, they will have little or no effect on the actual equilibrium curves. In the case of these  $H_2-N_2-CO$  mixtures, we are thus fortunate enough to be able to represent the phenomena within the plate column on a single triangular diagram for constant pressure and temperature. This greatly facilitates the theoretical treatment.

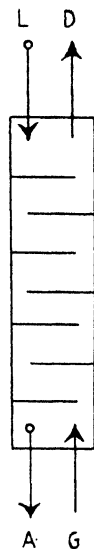


FIG. 136. Schematic scrubbing column

Now let us consider a scrubbing column, as shown schematically in Fig. 136. A saturated vapour  $G$ , containing hydrogen, nitrogen, and carbon monoxide, enters the bottom of the column, and pure liquid nitrogen  $L$  is introduced at the top. A vapour  $D$ , consisting almost entirely of hydrogen and nitrogen, leaves at the top, and a liquid carbon monoxide fraction  $A$  is withdrawn at the base.

Let  $x$  be the  $CO$ -concentration of a mixture and  $m$  its mass. Since the latent heats of evaporation of nitrogen and carbon monoxide (1,336 and 1,414 cal./mole respectively) are very similar, we can assume that the amounts of vapour and liquid are the same on each plate.

Then the  $CO$  balance equation for the column as a whole reads

$$x_A m_A - x_L m_L = x_G m_G - x_D m_D. \quad (1)$$

But according to our assumptions

$$m_A = m_L, \quad m_G = m_D, \quad x_L = 0.$$

Therefore

$$x_A = (x_G - x_D) m_G / m_L, \quad (2)$$

or, if we can assume that  $x_D \ll x_G$ ,

$$x_A = x_G m_G / m_L. \quad (3)$$

That is to say, if we introduce in a given time a known quantity of gas  $m_G$  with a known CO-content  $x_G$ , and if we specify the degree of purity  $x_D$  required and the amount of scrubbing liquid  $m_L$  used, the CO-content  $x_A$  of the liquid fraction is determined. On the other hand,

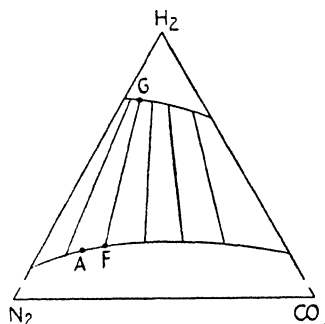


FIG. 137. Schematic equilibrium diagram of CO-N<sub>2</sub>-H<sub>2</sub> mixtures, showing what determines the minimum amount of scrubbing liquid

the liquid fraction  $A$  obtained cannot contain more CO than is in equilibrium with the ingoing vapour  $G$ . The composition of a liquid in equilibrium with  $G$  is given by the liquid end  $F$  of the connodal through  $G$  in Fig. 137. So if we specify  $m_G$ ,  $x_G$ ,  $x_D$ , and  $m_L$  and compute  $x_A$  from (2) or (3), the process will be feasible only if the value of  $x_A$  obtained, when plotted on the liquid branch of the equilibrium diagram, comes to lie to the left of point  $F$ , the end of the connodal through  $G$ . If  $A$  lies to the right of  $F$ , the specified conditions are incompatible with the functioning of the column. In this case,

to obtain the required purity at  $D$ , starting with a given quantity of composition  $x_G$ , we must use more liquid nitrogen. For by increasing  $m_L$ , while  $x_G$  and  $m_G$  remain constant, we can decrease  $x_A$  until  $A$  comes to lie to the left of  $F$ .

There will thus be a minimum amount of liquid  $\bar{m}_L$  which is essential to scrub out carbon monoxide from a given quantity of mixture of known composition, up to a specified degree of purity. This minimum amount of nitrogen will, of course, require an infinite number of plates. In practice, when a finite number of plates of efficiency less than unity is used,  $m_L$  will have to be greater than  $\bar{m}_L$ . Approximate calculations, made with the equilibrium curves of H<sub>2</sub>-N<sub>2</sub>-CO, showed that, to purify completely 100 cub. ft. of mixture containing 6 per cent. CO at  $-190^\circ\text{C}$ ., the minimum amount of liquid nitrogen needed varies between values corresponding to 9-12 cub. ft. of gas, according to the pressure used. The most advantageous pressure, from this point of view, is about 20 atm.

Now let us consider the number of plates needed for this process in conjunction with the amount  $m_L$  of liquid nitrogen. If we desire a

certain degree of purity and fix  $m_L > \bar{m}_L$ , a definite minimum number of plates is required, which can be ascertained in the following way. Suppose that equilibrium is attained on every plate, and consider an amount of vapour  $m_G$  with a CO-concentration  $x_G$ , which is to be freed from CO at a definite pressure and temperature. Take a certain value of  $m_L > \bar{m}_L$ , and a certain very small value of  $x_D$ , the CO-content of the final product.

Then

$$x_A = (x_G - x_D)m_G/m_L, \quad (2)$$

and  $A$  will lie to the left of the point where the connodal through  $G$  cuts the liquid branch of the equilibrium diagram.

$x_A$  is then the CO-content of the liquid leaving the lowest plate. According to our assumption, the vapour rising from this plate is in equilibrium with  $A$ . It will therefore be represented by the vapour end of the connodal through  $A$  (see Fig. 138).

We can determine the composition  $x_{A'}$  of the liquid leaving the second plate from below by writing down the balance equation for the whole column, excluding the lowest plate. This gives

$$x_{A'} = (x_G - x_D)m_G/m_L.$$

In this way the composition of liquid and vapour may be found successively for every plate until finally the CO-content has sunk to the value of  $x_D$ . The number of steps taken is equal to the minimum number of plates needed.

With this insight into the functioning of the scrubbing column we can find out whether or not scrubbing is identical with rectification. By determining the change in composition from plate to plate we have confirmed the conclusion drawn from the balance equation. Equations (2) or (3) now no longer merely give us the composition of the CO-fraction if it were possible to produce a product free from CO at the top of the column, but we now know that this product really can be attained.

Now the value of  $x_A$ , as obtained from (2) or (3), is quite independent of the shape of the equilibrium curves. It can be changed arbitrarily by varying one of the other independent variables, e.g.  $m_L$ , and  $m_L$  can always be so chosen as to satisfy the condition that  $x_A < x_F$ . Indeed,

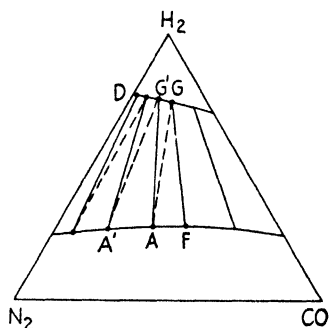


FIG. 138. Graphical determination of the number of plates required in a scrubbing column

by increasing  $m_L$ ,  $x_A$  can be made as small as we desire. The scrubbing will therefore be effective whatever the equilibrium curves look like, as long as they traverse the whole triangle and there is no critical point at the particular temperature and pressure. Scrubbing does not require a particular relationship between the vapour pressures of nitrogen and carbon monoxide. Indeed, if we call the  $N_2$ -content  $x$ , instead of the CO-content, we obtain exactly the same equations, and now  $x_A$  would

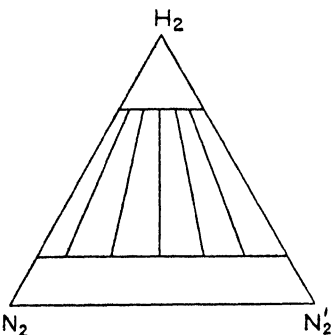


FIG. 139. Schematical equilibrium diagram of mixtures of hydrogen and two forms of nitrogen with identical thermal properties

have to be greater than  $x_F$ . If we wished, we could scrub out nitrogen with carbon monoxide as well as carbon monoxide with nitrogen. This proves that scrubbing is not identical with rectification. We could never reverse the position of oxygen and nitrogen in an air-separating plant.

Yet it would be wrong to say that rectification plays no part at all in the scrubbing process. To understand this, let us consider an imaginary ternary mixture, consisting of hydrogen and two substances with almost identical thermal properties, say two isotopes of nitrogen. The equilibrium diagram of such a system would be of the type shown in Fig. 139. The equilibrium curves would be horizontal straight lines and the connodals would be symmetrical in respect of the altitude of the triangle. We now know that there would be no difficulty in scrubbing out one of the nitrogen isotopes with the other.

Now let us consider the real ternary system. Its equilibrium diagram differs from the imaginary diagram just considered in two respects: the straight equilibrium lines become curves and the connodals are no longer symmetrical. The first is relatively unimportant, but the second is of greater interest. For the difference in the thermal properties of nitrogen and carbon monoxide lead to the fact that there is, as a rule, relatively more CO in the liquid than in the vapour, as compared with nitrogen. The connodals will therefore be turned somewhat in an anti-clockwise direction, as against the symmetrical connodals of the imaginary diagram. A glance at Fig. 138 shows that, for this reason, fewer steps will be required to scrub out CO with  $N_2$  than vice versa, fewer also than to scrub out one nitrogen isotope with another. Fewer plates will therefore be needed. The different thermal properties of nitrogen

and carbon monoxide thus facilitate the scrubbing process though they are not essential to it. An approximate numerical calculation shows that these properties cut down the number of plates required by about 30 per cent. This is a measure of the part played by rectification, in the strict sense of the word, in the scrubbing of a ternary mixture.

#### 4. The 'Air Liquide' process

The principal advantage of the Linde-Bronn process for separating coke-oven gas is that it yields a hydrogen-nitrogen mixture that is practically pure. The product frequently contains less than 0.01 per cent. CO and hardly a trace of other impurities. In view of the sensitivity of the catalyst to contamination with CO, this is of particular importance.

On the other hand, the plant described in § 2 is very unwieldy and complicated, especially owing to the large air-separating plant attached to it. This becomes very clear when we consider the course taken by the nitrogen passing through the aggregate. Nitrogen, in the form of atmospheric air, is first compressed and cooled to  $-190^{\circ}\text{C}$ . and separated from oxygen in the air column. It is then warmed up again and leaves the air column at room-temperature and atmospheric pressure. Thereupon it is again compressed, this time to 180 atm., again cooled to  $-190^{\circ}$ , and partly liquefied and put to its several uses in the coke-oven gas-separating plant. Again, part of the nitrogen remains pure and can be recompressed and circulated, but a considerable amount is lost in the CO-fraction, where it merely serves to lower the calorific value of the rich gas. All this renders the Linde-Bronn process less economical than could be desired.

Several attempts have been made to supplement the Linde-Bronn process by other methods, of which the Claude, or 'Air Liquide', process is the most famous. Claude evidently realized that it would be hardly possible to simplify or increase the efficiency of the Linde-Bronn process without decreasing the purity of the product. On the other hand, it is possible to dispense with high purity if the subsequent ammonia synthesis is carried out at very high pressures. In this case the catalyst is less sensitive to CO and, at very high pressures, the catalyst can be dispensed with altogether. By synthesizing at pressures of 800–1,000 atm., as against the 300 atm. used in the Haber-Bosch ammonia plant, Claude was able to use a hydrogen-nitrogen mixture containing considerable quantities of carbon monoxide. This greatly simplifies the separation of coke-oven gas and enables us to dispense with the scrubbing column altogether.

The elimination of the scrubbing column removes one important source of nitrogen consumption. Another disappears with the necessity of using liquid nitrogen as a refrigerant. According to Claude's well-known principle, all the refrigeration required is taken from the coke-oven gas itself, which is compressed to 25 atm., and then expanded in a cylinder. The high content of hydrogen in coke-oven gas, with its negative Joule-Thomson coefficient, renders the expansion of the gas in a nozzle ineffective from the point of view of refrigeration; on the other hand, it enables lower temperatures to be reached in a cylinder than could be attained with liquid air or nitrogen, especially when, as is the case with this plant, the less volatile constituents are removed before the expansion. Actually the temperatures prevailing behind the expansion cylinder are frequently as low as  $-210^{\circ}\text{C}$ .

In this way the only need for nitrogen is to bring about the stoichiometric composition for the synthesis of ammonia, and this nitrogen can be obtained from a small auxiliary plant.

The compressed coke-oven gas is first passed through a 5 per cent. solution of ammonia, which removes carbon dioxide, sulphuretted hydrogen, and other impurities. The ammonia vapour is then removed with water, and benzene is scrubbed out with mineral oil. The final removal of moisture and  $\text{CO}_2$  occurs in a series of drying towers filled with solid caustic soda. Thereupon the gas enters the low-temperature plant.

After traversing one of two alternate heat-exchangers *A* (Fig. 140), in which it is cooled with returning products to  $-65^{\circ}\text{C}$ ., the gas enters the first separating exchanger *B*, in which a fraction containing mainly ethylene condenses, including some propylene and ethane and a certain amount of methane. If desired, this fraction can be withdrawn in parts, one containing mainly ethylene, another mainly ethane, etc. Thence the gas, after passing through a small additional exchanger *C*, enters the tubes of a condenser *D* at about  $-100^{\circ}$ , in which the methane fraction is liquefied. The liquid fraction is expanded to atmospheric pressure and introduced between the tubes of the condenser. The gas, still containing some methane and most of the carbon monoxide, enters the tubes of a final condenser *E*, in which most of these constituents are removed. The liquid formed is again expanded and introduced into the condenser, whence it is drained off into *D*, mixing with the methane fraction. The upper part of *E* is separated from the lower by a horizontal partition between the tubes. A mixture, consisting almost entirely of  $\text{H}_2$  and  $\text{N}_2$ , but with rather more  $\text{CO}$  than in the case of

the Linde-Bronn apparatus, leaves the bottom of *E*, is slightly warmed in *C*, and enters the expansion engine *F*, where its pressure is reduced to 1 atm., the temperature falling to  $-200$ – $210^{\circ}\text{C}$ . This very cold gas forms the refrigerant in the upper part of *E*, which it leaves at about  $-170^{\circ}$ , and passes out of the plant through *B* and *A*. The methane fraction is utilized in the same fashion, precooling the ingoing gas.

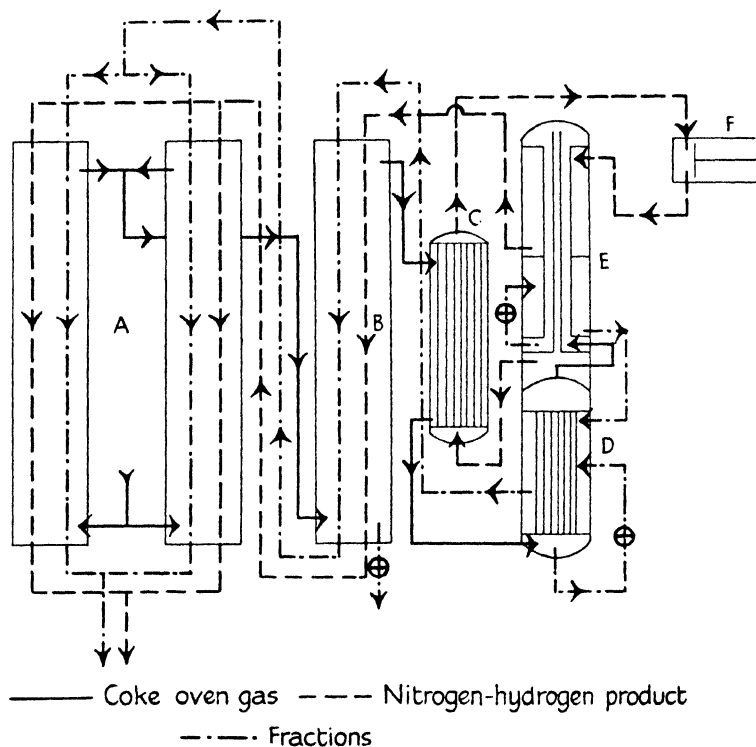


FIG. 140. The 'Air Liquide' process for separating coke-oven gas

The 'Air Liquide' plant exists in several variations, but in all the principal feature remains the expansion engine, which produces all the refrigeration and the very low temperature required to yield fairly pure products without scrubbing. The expansion engine is the only part of the plant erected outside the main lagged casing, and has the disadvantage of being sensitive and requiring some attention. As in all expansion engines working at low temperatures, the chief problem is lubrication. The lubricant in these engines is liquid nitrogen, which condenses in the cylinder and on the piston during the expansion stroke. Usually there is sufficient nitrogen to cover the requirements,



though a considerable quantity is lost in the methane fraction. Occasionally some nitrogen has to be added to improve the lubrication. The expansion engine is often coupled with a small electric generator and some use is made of the power gained. In very large plants it is coupled directly with the compressor. Never more than 30 per cent. of the work done in compressing a gas is regained in an expansion engine. In the case of coke-oven gas, when only about half the gas compressed actually passes through the expansion cylinder, the energy regained is much smaller.

The Air Liquide process for separating coke-oven gas is certainly simpler than the Linde-Bronn process, though the gas produced is not so pure. To a certain extent the simplicity is outweighed by difficulties encountered with the expansion engine. It is, however, probable that the progress made in recent years with expansion turbines will lead to the replacement of reciprocating engines by the much simpler rotary type. This is already beginning to influence low-temperature refrigeration, especially in large-scale apparatus, and should in future make it very much easier than heretofore to work industrial plant at temperatures even lower than that of liquid nitrogen.

## XI

### METHANE AND HELIUM

#### 1. Methane and its sources

METHANE is the oldest inflammable gas known. As marsh gas and earth gas it was a mystic substance in ancient times. As the centuries went by and more and more of this strange gas was found, as its constitution was determined and its physical and thermal properties studied, it remained much the same—a rather useless appendage of nature. Inert and intractable, chemical industry passed it by, and its occurrence in districts remote from dense centres of population effectively prohibited its use as fuel. Only a few small local industries drew their power from burning earth gas.

Methane in the form of natural gas was first utilized on a large scale in the United States, mainly for heating and lighting, and to-day the American annual output of  $2.5 \times 10^{12}$  cub. ft. is more than twenty times as great as that of all other countries together. The U.S.A. and Canada use more natural gas than coal gas; but even so only a fraction of the escaping gas is utilized. Much greater quantities are wasted.

The utilization of methane for domestic heating and lighting is particularly profitable in the U.S.A. It is the only highly industrialized country that has immense resources of natural gas, which, to all intents and purposes, is pure methane. This gas has a high calorific value and no injurious impurities. There is no object whatever in separating it into components. It is used as supplied by Nature.

Only in very recent times has methane begun to approach the field of this book, and it has not yet actually arrived there. But there are cogent reasons for believing that, at no very distant date, methane will play an important part in the gas-separating industry.

A general need for new resources of fuel on the one hand, and, on the other hand, the presence of vast resources of natural gas in and adjoining oil-fields, as 'wet', 'dry', and 'casing-head' gas, has faced the oil companies with the problem of marketing a gas that consists almost entirely of methane. And there are indeed a number of reasons suggesting that a demand for this gas may soon be created. For heating and lighting it has the advantage of a high calorific value (880 B.Th.U per cub. ft. as against the 500 B.Th.U. of town's gas), and as an engine fuel it has excellent anti-knock properties; a compression ratio of 16 : 1 can be reached without knocking. Its main disadvantage is that, as a

gas, it is difficult to transport overseas. Compression into cylinders is expensive and the cylinders themselves are heavy. A cylinder designed for a pressure of 150 atm. weighs about ten times as much as the methane it holds. The question has been raised in several countries of liquefying the methane and storing and transporting it in the liquid state. This is perfectly feasible, as will be shown presently, and the suggestion will probably be adopted sooner or later in most countries. In the U.S.S.R. it is already being applied.

This line of thought leads us to consider the liquefaction of methane but not its separation from other gases. For the natural resources that would be exploited for this purpose would consist almost entirely of methane, and any impurities occurring in the gas, such as ethane, propane, and even small quantities of nitrogen, could safely remain in the mixture.

The question of separation is raised from other considerations. It arises firstly from the desire in this and other countries for a home-produced fuel for internal-combustion engines, and secondly from the development of the gas industry. Granted that methane is an excellent fuel for engines, granted, too, that it may be handled in the liquid state, its occurrence as natural gas is limited to a few favoured countries. If it is to be produced in other countries, it must be taken from some other source. Once the value of methane is accepted, it is natural to consider what sources of methane are available.

Generally speaking, methane occurs everywhere where organic matter is subjected to thermal treatment, with or without high pressure. In the case of natural gas, this treatment has been supplied by Nature herself. As a result of human endeavour, methane is formed in the distillation and carbonization of coal, in town's gas and coke-oven gas. It is formed likewise in the cracking and hydrogenation of oil and coal; and finally it occurs in the fermentation of sewage. In the gases resulting from all these processes methane is present in varying proportions, but never in a state of purity. The production of pure methane from any of these sources entails the separation of a gaseous mixture and the application of the principles described in the preceding chapters. This question is now being considered seriously in several countries.

In the following table the principal sources of methane are listed, together with the approximate percentage of methane in the source and the approximate annual world production of the source in cubic feet, to the nearest power of 10.

TABLE 29. *The Sources of Methane*

<i>Source</i>	<i>% methane in source</i>	<i>World production (cub. ft.)</i>
Natural gas	70-100	10 <sup>12</sup>
Coke-oven gas	20-35	10 <sup>12</sup>
Coal gas	25-40	10 <sup>12</sup>
Cracker gas	30-45	10 <sup>11</sup>
Sewage gas	70	10 <sup>9</sup>
Hydrogenation gas	30-60	?

For countries such as our own, that are rich in coal, but possess no oil and little natural gas, the distillation or hydrogenation of coal affords the most obvious source of methane. Sewage gas, though it must be kept in mind, is probably not available in sufficient quantities. In most European countries, should methane be required, it will ultimately be obtained by the treatment of coal. This is quite in accordance with modern developments in the gas industry, where methods of complete gasification in connexion with hydrogenation can yield gases of widely varying methane content.

It is highly probable that, in the immediate future, one of the problems to be solved by scientists and engineers will be the production of methane, preferably in the liquid state, from a mixture of the type of coke-oven gas, but containing rather more methane and carbon monoxide and rather less olefines and nitrogen.

Before we consider a suitable process for producing methane from coal, it will be well to familiarize ourselves with the particular advantages accruing from its use in the liquid state and with the possible means for its liquefaction, as distinct from its separation from other constituents.

Methane is valuable from two distinct aspects—as an ingredient of high calorific value for town's gas, and as a high-quality non-knocking fuel for internal-combustion engines. For utilization in both these fields the question of storage is of paramount importance. The gas industry envisages methane firstly as a potential reserve in gas-making for use in periods of peak loads, to be diluted to standard calorific value possibly with water gas or nitrogen, or some other cheap gas of low calorific value the production of which is sufficiently elastic; and secondly as a possible substitute for town's gas, or, as is sometimes said, 'artificial natural gas'. This would imply a transition from the gas-consuming equipment prevalent in this country to that in use in the United States, where natural gas is the standard fuel for domestic heating. In both cases storage in the liquid state would offer considerable advantages.

Methane, as we shall see, is comparatively easy to liquefy, town's gas, which contains up to 50 per cent.  $H_2$ , is not. A tank  $20 \times 15 \times 10$  ft. could hold as much methane as a two-million cub. ft. gas-holder and would be immeasurably cheaper and less dangerous. If liquid methane can be produced cheaply enough, its storage in this form would be a great advantage.

As a fuel for internal-combustion engines, more especially for lorries, buses, and aeroplanes, methane has only one disadvantage, which is its bulk and, which comes to the same thing, the weight of high-pressure containers. If methane could be stored and transported liquid in tanks it would be just as good as petrol: its anti-knock properties are higher; its calorific value, expressed in calories per pound, is higher, and expressed in calories per gallon of liquid only slightly lower. Experiments carried out in the U.S.S.R. on a large scale and in England on a small scale have shown that liquid methane can be handled in cars to complete satisfaction.

Thus from every side we are brought to the conclusion that the future lies with liquid methane and not with the gas, provided liquefaction can be effected cheaply enough.

In Chapter V we considered the various methods of gas liquefaction as applied to air and their relative efficiencies and costs. The same calculations can be carried out for methane. The normal boiling-point of methane,  $112^\circ K.$ , is about  $30^\circ$  higher than that of air; at room-temperature its properties are further removed from those of a perfect gas than the properties of air. The result is that methane is easier to liquefy than air in the sense that its liquefaction requires the expenditure of a smaller amount of work. This is particularly evident when isenthalpic expansion is used, as in the Linde and cascade methods, which rely wholly on the deviations from the perfect gas laws. The advantage is less marked in the Claude and Heylandt processes, which are based partly on isentropic expansion; for here the efficiency is the greater the nearer the gas approximates to a perfect gas in the region of expansion. The position of methane as regards the law of corresponding states is particularly important for the case of cascade liquefaction; for whereas a four-stage cascade is needed to liquefy air with a high efficiency, a three-stage process is sufficient for methane. Ruhe-mann† found by calculation that the most efficient way of liquefying methane is with a cascade of three cycles, consisting of ammonia, ethylene, and methane, as shown in Fig. 141. The ammonia cycle

† M. Ruhemann, *Zhurn. khim. Prom.* **16**, 420 (1937).

works between 9 and 0.5 atm. abs., the ethylene cycle between 13 and 1, and the methane cycle between 25 and 1 atm. To liquefy 1 mole of methane, 1.8 moles must be circulated in the methane cycle, 2.0 moles in the ethylene cycle, and 0.7 moles in the ammonia cycle.

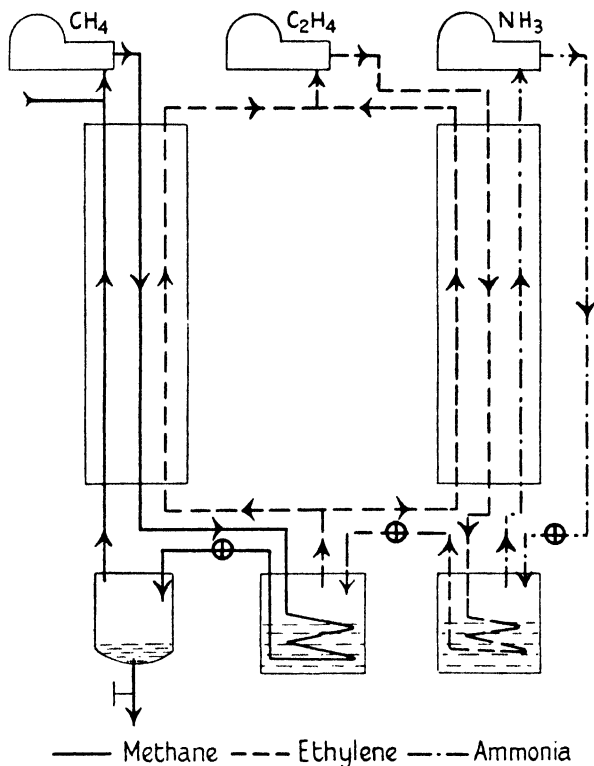


FIG. 141. Cascade for liquefying methane

Table 30 shows the work needed to produce 1 gallon of liquid methane, starting from pure gaseous methane at room-temperature and atmospheric pressure, with various possible cycles. The cycles were described in Chapter V.

TABLE 30. *Work needed to liquefy Methane with Various Cycles*

Type of liquefier	kWh. per gallon
Simple Linde cycle . . . . .	4.33
Heylandt cycle . . . . .	2.66
Linde high-pressure cycle . . . . .	2.59
Linde cycle with $\text{NH}_3$ -refrigeration . . . . .	2.07
Linde cycle with high pressure and $\text{NH}_3$ . . . . .	1.88
Ethane-methane cascade . . . . .	1.97
Ammonia-ethylene-methane cascade . . . . .	1.44

The figures given allow for probable losses in compressors and separating plant. If we take 2 kWh. per gallon as a rather pessimistic round figure and assume as the cost of power  $\frac{1}{2}d.$  per unit, the power cost of producing 1 gallon of liquid methane from pure gas is  $1d.$  This figure is certainly low enough to render the process economically feasible.

The figures given in the table refer to pure methane at room-temperature and 1 atm. They are therefore directly applicable in practice only to natural gas containing a very high percentage of methane. The presence of higher hydrocarbons in the gas would tend to reduce the figures somewhat, while nitrogen would tend to raise them.

We have, however, seen that, for most European countries, natural gas is not available as a source of methane for home production. Liquid natural gas would have to be imported in the same way that oil is imported to-day, and although this is possible, it does not solve the immediate problem of producing fuel at home. The table does, however, point to the fact that the production of liquid methane, from whatever source, is not a particularly costly process, though for thermodynamic reasons we can be sure that the cost must rise with decreasing methane content of the source.

It appears that the most likely source of methane in this country is a gas similar to town's gas, and calculations have been made to work out a method of producing methane from such a source. The well-known methods of separating coke-oven gas, as described in Chapter X, do not envisage the simultaneous production of methane. The various fractions are lumped together as rich gas and later utilized as such. Though it would be quite possible to keep the fractions separate, yet none of them, not even the so-called methane fractions, would be anything like pure methane. The Linde-Bronn fraction is heavily diluted with nitrogen and the Air Liquide fraction with carbon monoxide. Moreover, no provision is made for removing these fractions in the liquid state and, if this were done, it would alter the heat balance of the plant to such an extent that all the calculations would have to be started afresh.

The most probable mixture that would be forthcoming for methane production may be assumed to have roughly the following composition:

H <sub>2</sub>	.	.	.	.	50 per cent.
CH <sub>4</sub>	.	.	.	.	30 "
CO+N <sub>2</sub>	.	.	.	.	20 "

Moreover, this gas would probably be available at a pressure of between

30 and 50 atm. It is therefore natural to consider whether a sufficiently high percentage of the methane in the mixture can be liquefied by utilizing the available pressure drop. Calculations have been made to explore this possibility along the following lines.

We assume the pressure to be 40 atm., and, to simplify an otherwise very complex problem, consider a ternary mixture, consisting of 50 per cent.  $H_2$ , 30 per cent.  $CH_4$ , and 20 per cent.  $N_2$ . Owing to the great similarity in the thermal data of nitrogen and carbon monoxide, it is justifiable to expect that what is true for the one is equally true for the other, and since the properties of mixtures containing nitrogen are better known than those of mixtures with carbon monoxide, the gas described above was chosen as an example.

Since the uncondensable part of the mixture consists mainly of hydrogen, the pressure drop can best be utilized by expanding this part of the mixture isentropically in an expansion cylinder or turbine. For the properties of hydrogen approximate to those of a perfect gas very closely down to fairly low temperatures.

The proposed plant, which is sketched in Fig. 142, consists of two exchangers, a dephlegmator-condenser, and an expansion engine. The compressed mixture passes through both heat-exchangers and is partially liquefied in the second. It is then admitted at the base of the condenser and is further liquefied in the tubes. The liquid formed, consisting mainly of methane and nitrogen (carbon monoxide), is withdrawn from the sump of the condenser, expanded in a valve to atmospheric pressure, and admitted between the tubes. Hence a part, consisting mainly of methane, is drawn off; the rest evaporates and passes out through both heat-exchangers. The uncondensed part of the

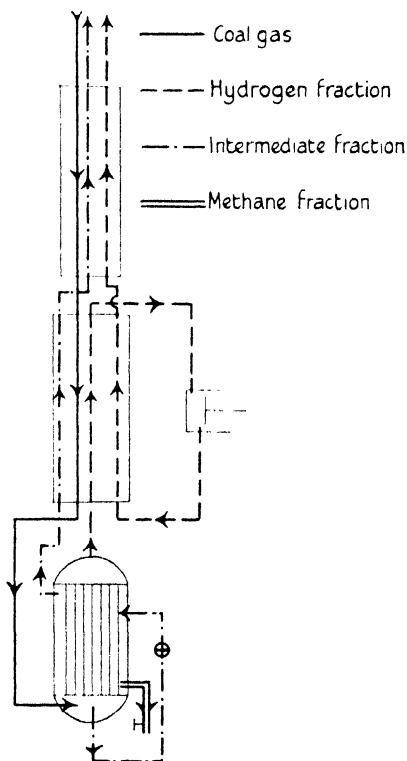


FIG. 142. Proposed plant for producing liquid methane from coal gas



mixture, consisting mainly of hydrogen and nitrogen (carbon monoxide), and still at 40 atm., passes through the cold heat-exchanger and thence through the expansion engine. At 1 atm. pressure it re-enters the cold heat-exchanger, which it traverses a second time, thus helping to condense part of the incoming mixture. Finally, it passes out through the warm heat-exchanger and leaves the plant at room-temperature.

It is possible to calculate somewhat approximately how this plant would work. Under the given conditions it appears that about 10 per cent. of the total amount of incoming gas could be withdrawn as a liquid, and this liquid would contain rather less than a third of the total amount of methane in the mixture. Its composition would be approximately 87 per cent.  $\text{CH}_4$  and 13 per cent.  $\text{N}_2$  (or  $\text{CO}$ ). This mixture could be further separated if required, but there are reasons to suppose that it might be desirable to maintain the composition as it is.

The calculation, inaccurate as it probably is, suffices to show that a rich liquid-methane fraction can be obtained from a gas of the specified composition, if the latter is available at 40 atm., without any further expenditure of energy. The residue of this process is essentially water gas and applicable as such. Whether the liquid methane obtained in this way is to be withdrawn as fuel for internal-combustion engines, whether it is to be stored as a reservoir of high calorific value for peak-load periods, or whether, as is quite possible, it will be reintroduced into the mixture after its excellent refrigerating properties have been utilized for some other purpose, is a problem for the future. At the moment it can only be stated that the production of liquid methane from coal is a definite possibility, offering considerable economic advantages to several industries.

## 2. Helium from natural gas

Apart from some weak sources containing considerable percentages of carbon dioxide, the principal constituents of all natural gases are light paraffins and nitrogen. Of the former, by far the most plentiful is methane, which is almost always present in far greater proportions than all other hydrocarbons together (see Table 6, p. 6). Even very 'wet' gases, closely associated with oil and to be considered as very light petrol, usually contain more than 80 per cent.  $\text{CH}_4$ . A gas like that of Ashland, Kentucky, consisting of 75 per cent.  $\text{CH}_4$ , 24 per cent.  $\text{C}_2\text{H}_6$ , and 1 per cent.  $\text{N}_2$ , is rather an exception.

On the other hand, a high nitrogen content is quite frequent among

natural gases, especially in those that occur remote from oil-bearing districts. In the U.S.S.R. gases containing 40 per cent.  $\text{CH}_4$  and 60 per cent.  $\text{N}_2$  are found far away from the oil districts, and similar mixtures are known in the U.S.A. (see Table 6).

But it was neither nitrogen nor methane that first led to the separation of natural gases. The component sought was helium. The overwhelming majority of natural-gas sources hitherto discovered contain no helium at all, or at least very little more than might reasonably be expected, assuming the nitrogen present to be due to atmospheric air. For the purpose of helium extraction, these gases offer no advantage over air. A small proportion of gases contain traces of helium up to 0.1 per cent., but it has never yet been found worth while exploiting them. A few gas wells, most of which are situated in the U.S.A., contain larger percentages of helium, varying from 0.1 to 1 or even 2 per cent. In most cases the helium content of rich sources decreases when large quantities of gas are drawn off.

The principal use to which helium is put is for the filling of airships. At the beginning of the last war it was generally believed that the airship was destined to play an important part in hostilities, and therefore great initiative was shown in exploiting the American and Canadian helium resources. Experience seems to show that these hopes, or fears, were exaggerated. The airship as an offensive weapon is no longer in the limelight.

However, the alleged destination of the helium has determined the outlook on its production. Airships are large; they need vast quantities of gas to fill them and still vaster reserves. If helium is to be produced at all it must be produced in large quantities. And if large quantities are to be produced, the sources must not only be rich in helium, but they must be large sources of gas.

The United States is the only country in the world that is known to have large sources rich in helium, and, until recently, when the U.S.S.R. took up helium production, the U.S.A. was the sole producer. Even the fairly rich Canadian sources were exploited for a short period only during the last war. The Americans have not found it worth while to produce helium from gases containing less than 0.5 per cent. With their rich sources they could afford to be fastidious. The Russians, on the other hand, whose sources, though large, are much weaker, are working helium plant on gases containing between 0.1 and 0.3 per cent. He.

Now it has been found that the richest helium sources are not the

gases closely associated with oil and consisting mainly of methane and ethane, but on the contrary those rather more remote from the oil fields, which contain a relatively high percentage of nitrogen. It is sometimes said that, the greater the nitrogen content, the greater the probability of finding a high percentage of helium. This is perhaps not strictly true, but it is a fact that where there is no nitrogen there is hardly ever helium. The figures of Table 6 give some impression of the connexion that appears to exist between helium and nitrogen; but it should be pointed out that these figures are somewhat arbitrary samples of a large number of tests and may therefore not be taken as a fair average.

The prevalence of nitrogen in helium-bearing natural gas is of considerable importance for the technique of helium production. For with a ternary mixture, consisting of methane, nitrogen, and helium, any separating process based on partial liquefaction will lead to methane liquefying first. Since the solubility of helium in liquid methane is very small, the liquid first formed may contain some nitrogen, but all the helium will remain in the gas. Methane and nitrogen are fairly easy to separate, and so the final stage of the process, and the only stage that offers any serious difficulties, will always consist in separating nitrogen and helium. This will hold quite irrespective of whether the original mixture contained 10 or 60 per cent.  $N_2$ . Thus, for the production of helium from natural gas, the methane is relatively unimportant, even though it may comprise up to 90 per cent. of the source. It may be of value as a refrigerant, but in the actual separating process we always have to deal with an essentially binary mixture, consisting of helium and nitrogen.

Let us consider such a binary system. The boiling-points of its components lie very far apart. The vapour-liquid equilibrium curves are known (see Figs. 50 and 51). We have already discussed the system in an example in Chapter III and there would appear to be no difficulty in effecting a complete separation by the method of partial liquefaction.

And yet the operation is not quite so straightforward as we might imagine. One difficulty becomes apparent as soon as we consider the purity of the helium to be produced. If this is to be 99 per cent., as is usually required, a considerable strain is put upon the efficiency of the separating plant. The normal boiling-point of nitrogen is  $77.3^\circ K.$ , and liquid nitrogen is the coldest refrigerant naturally available. With a refrigerant boiling at  $77^\circ$ , the temperature of the mixture cooled cannot easily be maintained below  $80^\circ K.$  But to remove almost all

the nitrogen from a helium–nitrogen mixture at 80° K., fairly high pressures are required. The following are the helium concentrations of vapours in equilibrium with liquids at 80 and 70° K. at various pressures.

TABLE 31. *Helium–Nitrogen Mixtures*

<i>p</i> (atm.)	% He in vapour at equilibrium	
	% He at 80°	% He at 70°
10	79	93
20	91	98
40	95.5	99.2
60	97.2	99.6
100	98.5	..

We see that, even at pressures as high as 100 atm., the highest purity obtainable at 80° is 98.5 per cent. He. Even apart from the fact that this high pressure is impracticable for other reasons, it is clear that at 80° pure helium cannot be obtained; for we cannot expect complete equilibrium to be reached. Evidently we must either use a refrigerant with a still lower temperature, or we must apply some additional method of purification, such as fractional adsorption on charcoal or the like. At 70° K., a temperature that can be maintained with liquid nitrogen boiling under reduced pressure, conditions are better. The table shows that pressures of about 40 atm. should be sufficient to obtain helium of 99 per cent. purity.

Thus low temperatures and fairly high pressures are required to produce pure helium from a mixture with nitrogen. But here another difficulty arises, owing to the solubility of helium in liquid nitrogen. As may be seen from Figs. 50 and 51, this solubility is not very great, especially at low temperatures, but we must remember that we are dealing with weak helium sources. When the original mixture contains only a small proportion of helium, a liquid containing a few tenths of a per cent. will already lead to considerable losses. Suppose the original mixture contained 2 per cent. He, 40 per cent. N<sub>2</sub>, and 58 per cent. CH<sub>4</sub>. Let us assume that we have removed all the methane in a fraction consisting of 90 per cent. CH<sub>4</sub> and 10 per cent. N<sub>2</sub> and no helium. The remaining gas, consisting only of nitrogen and helium, is then partially condensed, leaving a vapour containing 99 per cent. He. If the liquid fraction has 0.5 per cent. He dissolved in it, it means that 8.5 per cent. of the total helium present in the original mixture is wasted. The position becomes still more precarious when very weak mixtures are treated, and this is probably one of the reasons why these

are not used in the United States. However, it has been possible to produce large quantities of pure helium from sources containing less than 0.3 per cent. He with very slight losses. This was achieved by a careful study of the separating process.

Dephlegmators and plate columns have been used to separate helium from nitrogen and methane and occasionally a combination of the two. There is apparently some uncertainty as to which are preferable, and the general opinion seems to be that, as the plate column is on the whole the stronger weapon, it should be applied in this rather difficult case. Actually the advantages of the plate column lie in its ability to separate substances whose boiling-points are close together, such as nitrogen and oxygen or nitrogen and carbon monoxide. For mixtures with widely differing boiling-points, like nitrogen and helium, they have few advantages over dephlegmators. At first sight it might appear that they would be useful in preventing loss of helium dissolved in liquid nitrogen, but we shall see that this danger is smaller than might have been thought. A series of dephlegmators, correctly handled, are quite capable of producing helium of 99 per cent. purity with a very high yield, which precludes any extensive losses of helium through solution in liquid fractions.

Though the action of a dephlegmator has been described in Chapter III, using air as an example, it will be well to consider it again at this point, as applied to a mixture of nitrogen and helium. Suppose the mixture to be precooled in such a way that it enters the tubes of a dephlegmator from below as a saturated vapour. We assume that a suitable liquid refrigerant is boiling between the tubes. Then nitrogen will condense in the tubes and trickle down into the sump, as described in Chapter III. We have seen that the purity of the more volatile component, in our case helium, is determined by the temperature of the refrigerant. The highest purity obtainable is given by the composition of a saturated vapour at the given pressure and at the temperature of the refrigerant. In the case of oxygen-nitrogen mixtures, the purity of the nitrogen can be raised as high as we like. If the temperature of the refrigerant is below the boiling-point of nitrogen at the pressure of the mixture, and if the dephlegmator is sufficiently long, the nitrogen emitted at the top of the dephlegmator will be pure. In the case of helium-nitrogen mixtures, owing to the peculiar shape of the equilibrium curves at temperatures high above the critical temperature of helium, the purity is determined by the temperature and pressure according to Table 31 on p. 261. But the liquid collecting in the sump

of the dephlegmator cannot contain less helium than is in equilibrium with the ingoing vapour. It will, in fact, always contain rather more than this amount.

Now consider a  $(T, x)$  diagram of helium–nitrogen mixtures, e.g. that for 20 atm. shown in Fig. 51. The mixture entering the dephlegmator will contain only a few per cent. of helium. The vapour curve is so flat that the composition of a liquid in equilibrium with any vapour will always lie close to the point where the two curves meet at a sharp angle; and the weaker the original helium–nitrogen mixture, the lower will be the helium concentration in the liquid. In the example given above of a 2 per cent. He source, the helium–nitrogen mixture obtained after removing the methane would contain 5.6 per cent. He. A liquid in equilibrium with this vapour contains about 0.2 per cent. He, i.e. much less than the 0.5 per cent. that we assumed. And with a weaker mixture the losses would be proportionally smaller. It is thus clear that losses can be kept down by arranging for a suitable temperature of the incoming gas at the base of the dephlegmator, whereas to secure a high purity of the product, the temperature of the refrigerant between the tubes of the dephlegmator must be kept as low as possible.

In practice the separation of pure helium from mixtures containing methane and nitrogen is usually effected in two stages. In the first most of the methane and nitrogen is removed and the helium content is increased to anything between 5 and 30 per cent. This can be achieved at fairly low pressures of a few atmospheres. The rich mixture is thereupon warmed up and compressed to some 30 or 40 atm. and pure helium is then produced in the second stage.

The plant consists of a series of units, which may be dephlegmators or plate columns or an assortment of each. The original plant at Fort Worth, U.S.A., consisted mainly of plate columns, the Canadian plant at Calgary was a combination of plate columns and dephlegmators, and a plant in South Russia is composed of dephlegmators alone.

Most existing works are in a continual state of renewal and alteration, and this held also for the plant that has gone out of use. Instead of giving an accurate description of any single helium plant, we shall therefore sketch a typical plant consisting of four dephlegmators. A plant very like that shown in Fig. 143 was certainly working a few years ago.

The natural gas is compressed to the pressure necessary to supply the refrigeration, which will vary according to the size of the plant. It is then cooled and partially liquefied in two or more exchangers with

cold returning vapours. Part of the gas is expanded in a cylinder behind the first heat-exchanger, the rest, together with the liquid already formed, is passed through a throttle valve. Liquid and vapour

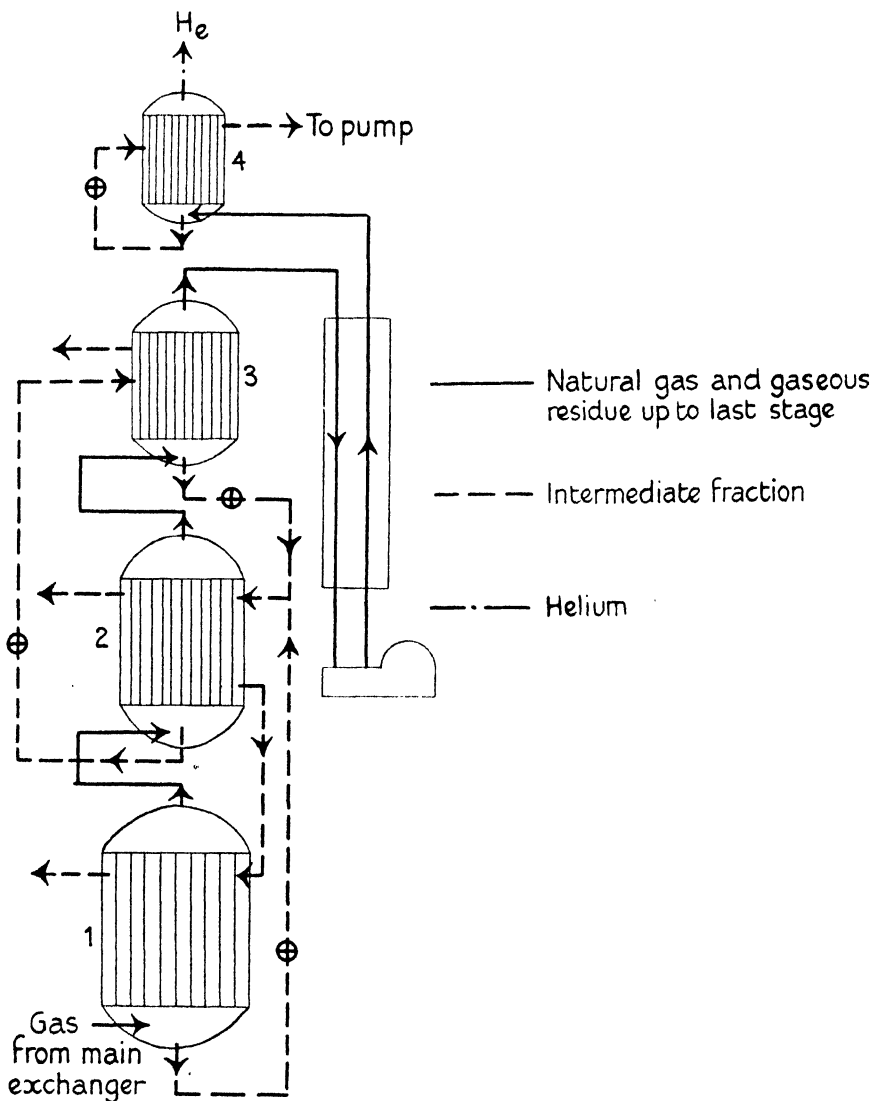


FIG. 143. Plant for separating helium from natural gas

together thereupon enter the first dephlegmator (1) at an intermediate pressure. The uncondensed portion is then passed on to the second dephlegmator (2) and thence to the third (3). The liquid mixture of methane and nitrogen, collecting in the sump of (1), the composition

of which will depend on that of the source, is expanded to atmospheric pressure and introduced between the tubes of (2), whence part of it overflows into (1). The liquid formed in the tubes of (2), which will consist mainly of nitrogen, is admitted after expansion between the tubes of (3). Almost pure liquid nitrogen, formed in the sump of (3), is added to the refrigerant supplied to (2). The refrigerants evaporating from all three units serve to cool and liquefy incoming gas. If the pressure of the mixture in the tubes of (3) is not far above 1 atm., the vapour escaping from the refrigerant is pumped off with a vacuum pump to lower the temperature. But if this pressure is maintained at 10 atm. or higher, this is not necessary. In any case, the refrigerant in (1) is warmer than that in (2) and the latter is warmer than that in (3), since the methane content of the liquids decreases from one unit to the next. The rich gaseous He-N<sub>2</sub> mixture emerging from the summit of (3) may contain 5 per cent. He, as is the case in the corresponding unit of the Canadian plant, or 30 per cent. He, as in one of the Russian plants. This depends on the pressures at which this part of the apparatus is worked. The higher the pressure in the tubes of the dephlegmators, the higher the helium content in the intermediate product and the smaller its quantity, i.e. the greater the achievement in the first stage of the process.

The enriched helium gas is now warmed up and recompressed to a pressure between 30 and 50 atm. It is then cooled down and partially liquefied in a series of exchangers and introduced into the sump of the fourth dephlegmator (4). The liquid is expanded to a pressure of one-quarter or one-fifth of an atm. abs., maintained by a strong vacuum pump, and admitted between the tubes of (4), where it boils at a temperature which may be as low as  $-207^{\circ}\text{C.}$  ( $66^{\circ}\text{K.}$ ). The final product, emerging at the top of (4), has a helium content that varies from 97 to 99 per cent., according to the dimensions of the dephlegmator and the pressures inside and outside the tubes.

The dephlegmators become smaller and smaller as the separation proceeds, and the product of (4) is so small that it is not worth while passing it through the exchangers.

Very pure helium—up to 99.5 per cent.—can be obtained with this type of plant, but it is sensitive to small changes in régime and the valves need careful adjusting. Changes in the composition of the crude gas are particularly disturbing, and these frequently occur when the pipe-lines are supplied from several blow-holes simultaneously, each of which varies in strength. The power consumption per cubic foot of pure



helium is considerable and only in a large aggregate can helium be produced moderately cheaply. The costs can be lowered by using the methane fraction from the first dephlegmator, or the natural gas itself, if it has a high methane content, to drive the engines. American helium, shortly after the last war, could be purchased for about 6*d.* per cubic foot. During one period, somewhat later, the price had dropped to 2*d.* But as the production and sale is strictly controlled—at some periods no helium is sold at all—it is difficult to assess the true cost of production.

## XII

### THE SEPARATION OF OLEFINES FROM CRACKER GAS

#### 1. The principles of separation

THE cracking and pyrolysis of oil, with a view to increasing the quantity and improving the quality of the petrol in the crude oil, has added very materially to the world resources of combustible gas. About 20 per cent. by weight of the petrol produced is emitted as gas, most of which is used for industrial heating on the spot or passed into the gas mains. As much as 80 per cent. of heavy oil can be converted into petrol by cracking. Almost  $10^{10}$  gallons of petrol are produced annually by cracking in the U.S.A. together with about  $3 \times 10^{11}$  cub. ft. of gas. The annual production of cracker gas is thus not far behind that of coal and coke-oven gas.

The composition of cracker gas differs considerably according to the conditions of pressure and temperature in the cracking plant and according to the properties of the crude oil. But in every case the composition is very different from that of the gases hitherto discussed. Cracker gas is characterized by a high percentage of unsaturated hydrocarbons of the olefine series and the almost complete absence of carbon monoxide and nitrogen. Cracker gas is essentially a mixture of hydrogen and hydrocarbons. Industrially, the importance of cracker gas lies in its high olefine content, since olefines are growing more and more valuable as basic substances for chemical synthesis. The production of pure olefines from cracker gas is therefore rapidly becoming an important large-scale industry.

The separation of olefines from cracker gas is the most intricate problem of industrial gas separation. Though it is carried out according to the same principles as the processes already discussed, it necessitates the use of rather complicated plant, giving rise to involved flow-sheets.

The difficulties encountered are due to three main causes.

1. Cracker gas is not even approximately a binary system. As can be seen from Table 7, p. 7, it contains five or six constituents in percentages from 6 to 30. None of these can reasonably be neglected, even for rough calculations.
2. Whereas hitherto, with the exception of argon, we were always interested in those components of a mixture with the highest or lowest boiling-points, we are here seeking to separate off components with intermediate boiling-points. The boiling-points of ethylene and

propylene are higher than those of methane and hydrogen and lower than those of propane, butane, etc.

3. If we arrange the constituents of cracker gas in the order of their boiling-points, there are always one or more paraffins between two olefins. Thus the boiling-point of ethane lies between those of ethylene and propylene. Propane and iso-butane lie between propylene and the butylenes, etc. It is therefore not possible to obtain fractions from cracker gas containing olefins only and then to separate the olefins from one another. There is always an intervening paraffin to complicate the process. This is illustrated in Table 32.

TABLE 32. *The Constituents of Cracker Gas and their Boiling-points*

<i>Constituent</i>	<i>Formula</i>	<i>Boiling-point (°C.)</i>
Hydrogen	H <sub>2</sub>	—252.5
Methane	CH <sub>4</sub>	—161.6
Ethylene	C <sub>2</sub> H <sub>4</sub>	—103.0
Ethane	C <sub>2</sub> H <sub>6</sub>	—88.7
Propylene	C <sub>3</sub> H <sub>6</sub>	—47.0
Propane	C <sub>3</sub> H <sub>8</sub>	—42.2
Iso-butane	C <sub>4</sub> H <sub>10</sub>	—12.2
Iso-butylene	C <sub>4</sub> H <sub>8</sub>	—6.6
<i>n</i> -butylene	C <sub>4</sub> H <sub>8</sub>	—6.1
<i>n</i> -butane	C <sub>4</sub> H <sub>10</sub>	—0.6
$\alpha$ -butylene	C <sub>4</sub> H <sub>8</sub>	+1.0

The separation of cracker gas with a view to obtaining pure olefins is therefore difficult, alike from a practical and from a theoretical point of view. It has been taken up first, as was to be expected, in the U.S.A. and the U.S.S.R., the two principal oil-producing countries having at the same time a highly developed chemical industry. A large number of processes have been devised, which differ very considerably from one another. These differences refer to the type of fractions produced and to the sources of refrigeration employed; moreover, the details of the plant naturally depend on whether ethylene only is to be obtained, or whether pure propylene and higher olefins are also desired.

In every case, even in the simplest plants, several units are required, which may be dephlegmators or rectifying columns or combinations of the two. Each of these units necessitates the introduction at some point or other of a liquid fraction or the condensation of considerable quantities of vapour in a condenser-evaporator. In each unit condensation must be effected at a definite temperature, and in no two units

will this temperature be the same. This immediately raises the question of suitable refrigerants.

From this point of view, the various methods of separating cracker gas can be divided into two classes: those that employ 'foreign' refrigerants and those that use as refrigerants only the various fractions occurring in the plant. In the latter case, all the refrigerating effect required must be obtained by compression and expansion of the cracker gas itself or one or another of its fractions. This is the type of plant developed recently by the Air Reduction Co. in New York. On the other hand, in certain American and Russian aggregates, free use is made of 'foreign' refrigerants, notably ammonia. But apart from this, it has been found useful to apply an independent ethylene cycle to produce refrigeration at lower temperatures. In some cases propane is used to replace or supplement ammonia.

As the demands on the purity of the products increase, it is found necessary to lower the temperatures at which separation is effected. Thus, to prevent measurable quantities of ethylene being lost in the vapour residue of lighter constituents (hydrogen and methane), it is usually necessary to scrub the vapour with liquid methane. This requires that, at some point, the temperature be lower than the boiling-point of methane at the pressure obtaining in the plant. This temperature can be raised to about  $-90^{\circ}\text{C}$ . by increasing the working pressure, but this, as we know, hinders separation and entails additional power consumption for compressing the gas. Though some columns are made to work at 30 atm. or over, the latest American aggregates are built for pressures between 10 atm. and 15 atm. and correspondingly lower temperatures. Part of the gas or gaseous fractions is sometimes brought to a higher pressure in order to supply the refrigeration needed.

Two types of separating plant can further be distinguished by the way the initial gas is divided into fractions or, to use a term from oil distilling, by the method of cutting. Suppose we wish to obtain pure ethylene. Then, according to one type of plant, we first separate the mixture into a liquid fraction containing ethylene and components with higher boiling-points and a vapour containing only components with lower boiling-points than ethylene (methane and hydrogen). The liquid is then separated into a vapour consisting of pure ethylene and a liquid consisting of all the less volatile components. This is technically the simplest procedure, but in practice it is usually not possible to remove all the ethylene from the vapour in the first cut, and thus some ethylene is wasted. The principle is shown diagrammatically in Fig. 144, No. 1,

where the variously marked squares symbolize certain mixtures or components, as explained under the figure. An example of a plant functioning in this way will be given presently.

In the second type of plant, the initial mixture is first separated into a vapour containing ethylene and more volatile components and a liquid

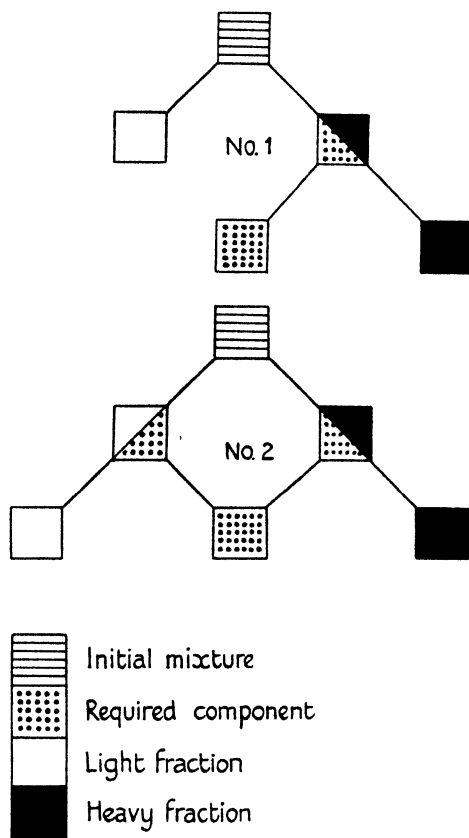


FIG. 144. Diagrams showing stages in separating cracker gas

containing ethylene and less volatile components, as shown in Fig. 144, No. 2. The liquid and the vapour are then each separated again, the former into pure ethylene vapour and a liquid consisting of all the less volatile constituents, the latter into pure liquid ethylene and a vapour containing only methane and hydrogen. This method is very pleasing in its symmetry in the diagram, but is not necessarily more efficient than the first. In practice the arrangement is not always quite as straightforward as in the diagram, as we shall see when we come to discuss an actual plant.

When more than one olefine is to be separated, we can repeat the same process with the residual mixture of components having higher boiling-points than ethylene. In this case the plant naturally becomes rather more complicated.

## 2. Separating plant for cracker gas

We shall first consider a Russian plant, using foreign refrigerants. Separation is effected at 30 and 25 atm. in two rectifying columns. The refrigerants used are ammonia, boiling at reduced pressure, and a closed ethylene cycle, as well as liquid ethylene obtained in the separation process. The plant is actually used to produce ethylene, propylene, and higher olefins, but we shall discuss only the parts for separating ethylene.

The process is shown schematically in Fig. 145, in which the compressor and purification plant have been omitted. We assume that moisture and traces of carbon dioxide, as well as small quantities of benzene and toluene, have been removed.

The cracker gas, compressed to 30 atm., first traverses the main heat-exchanger  $E_1$ , in which it is cooled by all three outgoing products—a mixture of methane and hydrogen, almost pure ethylene, and a residue consisting of components with higher boiling-points than ethylene. It is then further cooled in the ammonia heat-exchanger  $N$  and in an additional heat-exchanger  $E_2$  in counter-current with the methane-hydrogen mixture.

The compressed gas leaves  $E_2$  at about  $-50^\circ\text{C}$ . and is admitted, partially liquid, to the middle of the 'cold column'  $C$ , in which methane and hydrogen are removed from it. The column has two condensers in series, shown in the figure separately and distinct from the column. The first  $K_1$  is fed with liquid ethylene from the closed ethylene cycle (not shown in the figure), the second  $K_2$  with liquid ethylene obtained from the cracker gas. The temperature of the condensed effluent returned from the condensers is about  $-90^\circ\text{C}$ . The evaporator at the bottom of the column  $C$  is heated with an external source to  $+10^\circ\text{C}$ . The vapour leaving the summit of  $C$  is a mixture of hydrogen and methane; the liquid returned from the condensers is almost pure methane. It serves to scrub out ethylene from the rising vapours. As no methane leaves the column except from the top, the effluent ultimately leaving  $K_2$  and returned through  $E_2$  and  $E_1$  contains the same ratio of methane to hydrogen as the original mixture (about 2.2:1). But in view of the condensation of methane in the condensers and its

readmission to the column, its concentration in the upper part of the column, under stationary conditions, is very high. Even so the effluent still contains 2–3 per cent.  $C_2H_4$ , which is thus lost in the process.

The liquid fraction collecting in the sump of the column *C*, which contains all the rest of the ethylene and practically no methane or

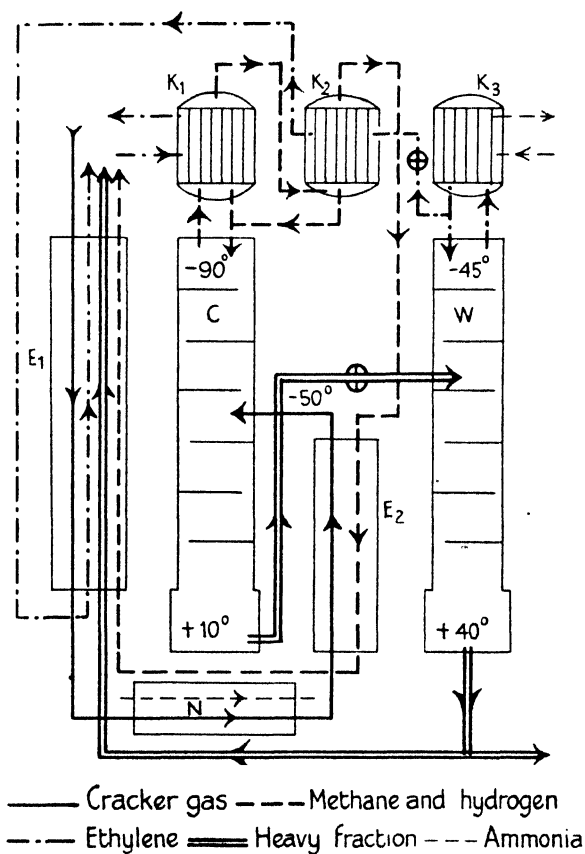


FIG. 145. Russian plant for separating cracker gas

hydrogen, is expanded from 30 to 25 atm. in a valve and then admitted to the middle of the 'warm column' *W*. The condenser  $K_3$  of this column is fed with liquid ammonia boiling at reduced pressure at a temperature of about  $-45^\circ C$ . The sump is heated with steam to  $+40^\circ C$ . In *W* the fraction is separated into a vapour consisting of 99 per cent.  $C_2H_4$  and a liquid consisting of all the components with boiling-points above that of ethylene together with about 2 per cent.  $C_2H_4$ , which is lost. Part of the ethylene liquefied in  $K_3$  is readmitted

as reflux to  $W$  and serves to scrub out ethane and higher hydrocarbons; the rest is transferred as refrigerant to  $K_2$ , after being expanded to atmospheric pressure. The ethylene vapour evaporating from  $K_2$  is withdrawn through the main heat-exchanger  $E_1$ .

The liquid fraction formed in the sump of  $W$  is either returned directly through  $E_1$ , or is transferred to a third column (not shown in the figure) for the separation of propylene.

In this plant about 85 per cent. of the ethylene present in the original cracker gas can be obtained. The flow-sheet is relatively simple, but the necessity of using auxiliary ethylene and ammonia cycles adds certain complications. These are, however, not greater than those in the other plants to be considered. The power consumption for this and other aggregates is not known, and the available data are insufficient to justify a calculation at this stage.

It is interesting to compare this plant with one described by the Air Reduction Co. in New York in 1934, the purpose of which was to obtain ethylene only. Here no foreign refrigerants are used and no attempt is made to remove all the methane and hydrogen at the first cut, leaving all the ethylene in the fraction together with components of higher boiling-point. The arrangement corresponds to No. 2 in Fig. 144, and not to No. 1, as in the plant previously described. The pressure of the incoming gas is not specified, as it depends on its composition. The arrangement is shown in Fig. 146.

It consists in the main of two plate columns  $C$  and  $W$ , each of which is divided into two parts by a condenser in the middle. A dephlegmator is inserted at the bottom of each column, surrounded by baffle trays of the type described in Chapter III.

After passing through the main heat-exchanger  $E_1$ , in which it is cooled by all three products, as in the previous plant, the compressed cracker gas is admitted at the bottom of the dephlegmator  $D_w$  of the column  $W$ , where it is partially condensed with the help of a fraction to be described later. In  $D_w$  a preliminary separation occurs, which is not assumed to be very effective. The liquid fraction consists essentially of ethylene and constituents with a higher boiling-point, and the effluent contains ethylene and more volatile components. But small quantities of methane may be dissolved in the liquid and small quantities of ethane may remain in the vapour.

The liquid fraction is expanded to an intermediate pressure into the trap  $T$ , in the course of which part evaporates, including all the methane. The liquid residue is expanded to approximately atmospheric



pressure and delivered near the bottom of the upper section of the column  $W$ . It now consists only of ethylene and constituents of higher boiling-points.

The vapour withdrawn from the top of  $D_w$  is transferred, still at high pressure, to the bottom of the dephlegmator  $D_c$  in column  $C$ . Here it

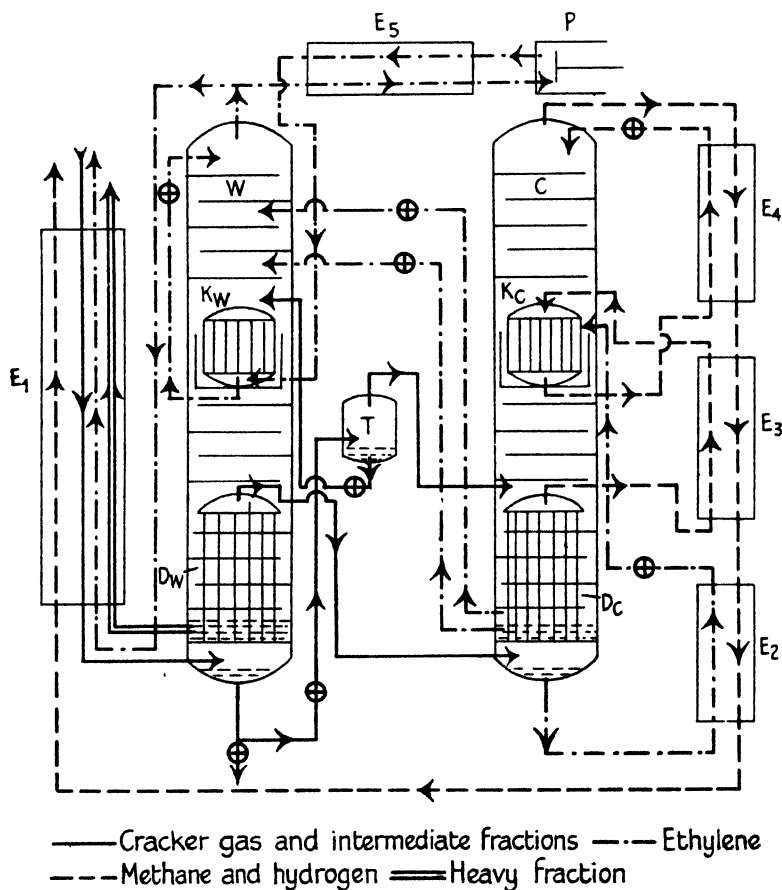


FIG. 146. American plant for separating cracker gas

is separated into a vapour consisting only of methane and hydrogen, and a liquid fraction containing ethylene and small traces of components with higher and lower boiling-points. The liquid is supercooled in an exchanger  $E_2$  with the help of cold hydrogen-methane vapour, expanded to an intermediate pressure, and admitted to the bath around condenser  $K_c$  in  $C$ . From here part of it flows over into the lower part of  $C$ , passes over the lower plates, and trickles down the baffle trays,

finally collecting around  $D_c$ . This liquid fraction has now lost all traces of methane and consists of ethylene with small amounts of less volatile components.

Liquid and vapour from the bottom of  $C$  are expanded to low pressure and introduced in the middle of  $W$  above the fraction already described.

In this way, all fractions containing ethylene and less volatile components are united in  $W$ , the methane and hydrogen having been removed. To complete the separation of ethylene, two processes are still required: the constituents with higher boiling-points must be scrubbed out of the ethylene in  $W$ , and the ethylene itself must be scrubbed out of the methane-hydrogen effluent in  $C$ . For this purpose a reflux of liquid ethylene must be supplied at the top of  $W$  and a reflux of liquid methane at the top of  $C$ .

The ethylene reflux is obtained as follows. Part of the ethylene effluent from  $W$  is branched off before the main heat-exchanger  $E_1$  and warmed up to room-temperature in an exchanger  $E_5$ . It is then compressed to about 100 atm. in the compressor  $P$ , cooled again in the same exchanger  $E_5$ , and liquefied in the condenser  $K_w$  in  $W$  with the help of the fraction transferred from the sump. The liquid, which should be very pure ethylene, is expanded to 1 atm. and admitted at the top of  $W$ . The final effluent from  $W$ , apart from the recompressed portion, is withdrawn through  $E_1$ . The function of the compressor is to supply additional refrigeration and thus to replace the ethylene and ammonia cycles, used in the plant described previously.

The methane reflux is obtained by condensing part of the hydrogen-methane effluent from  $D_c$  in the condenser  $K_c$  in  $C$ , after cooling it in an exchanger  $E_3$  with the help of cold hydrogen-methane vapour. It is then further cooled in  $E_4$ , expanded to the intermediate pressure obtaining in  $C$ , and admitted at the top of the column. The effluent from  $C$ , consisting of methane and hydrogen only, is returned through  $E_4$ ,  $E_3$ , and  $E_2$ , and finally through the main heat-exchanger  $E_1$ .

The purity of the ethylene obtained from this plant is given as 99 per cent., which is the same as that previously described. We have no information as to the yield, but it is probably slightly higher than that of the Russian plant. Its chief advantage lies in the fact that no foreign refrigerants need be employed.

If we study the flow-sheet and the whole conception of this plant, we are forced to conclude that the separation of pure ethylene from cracker gas is an arduous and complicated process, at any rate if a high

yield is desired. A comparison with the general scheme, outlined in No. 2 of Fig. 144, shows that, in practice, the process is more complex than the diagram might lead us to expect. The simple cut, envisaged as the initial stage of separation, is evidently not possible in a dephlegmator. We cannot separate in this way a gaseous phase containing only ethylene, methane, and hydrogen, and a liquid phase containing only ethylene and less volatile components. The insertion of the trap *T* indicates that some methane is present in the heavier fraction, and the readmission of liquid ethylene in the centre of the upper part of *W* shows that it contains a certain amount of ethane. The difficulty of separating ethylene and ethane is clear from the shape of the equilibrium curves of the ternary methane-ethylene-ethane system in Fig. 47. Here most of the liquid curves are almost horizontal and the connodals fairly symmetrical about the methane axis.

The most characteristic point in the plant, and where it deviates from the simple diagram, is the transfer of the liquid fraction from *C* to *W*. The final purification of the ethylene is carried out in the presence of *all* the constituents with higher boiling-points in a single process, after all the methane and hydrogen have been removed in *C*. Moreover, just as no foreign refrigerants are required, no external heating is needed in this plant. Since the pressure in the column *W* is near to 1 atm., the temperature at which the final separation of ethylene occurs is much lower than in the other plant. All the heat required is supplied by the condensing fractions in  $D_w$ ,  $D_c$ ,  $K_w$ , and  $K_c$ .

Finally, let us consider an American plant for separating ethylene and propylene from cracker gas simultaneously. The process was developed by the Air Reduction Co. and patented in 1936. As in the plant last described, no foreign refrigerants are used; the refrigeration required is obtained by recompressing gaseous fractions and, in one case, expanding gas in a cylinder.

The essential feature of this plant is the simultaneous production of two liquid fractions and a gaseous effluent in the initial stage of separation. One fraction contains all the propylene and no ethylene, the other no propylene and the major part of the ethylene. The rest of the ethylene, with some ethane, escapes temporarily with the gaseous effluent. The cut between the two liquid phases is thus effected through the ethane, which is contained in both fractions. This is facilitated by the use of a rectifying column in the initial stage, as against the dephlegmator used in the last case. A plate column allows sharper cuts to be made than are possible in other types of apparatus.

The process is illustrated diagrammatically in Fig. 147 and the flow-sheet is shown in Fig. 148.

The cracker gas, compressed to about 12 atm., after traversing the main heat-exchanger  $E_1$ , in which it is partially liquefied, enters the middle of the lower part of column  $C$ , which is fitted with an evaporator

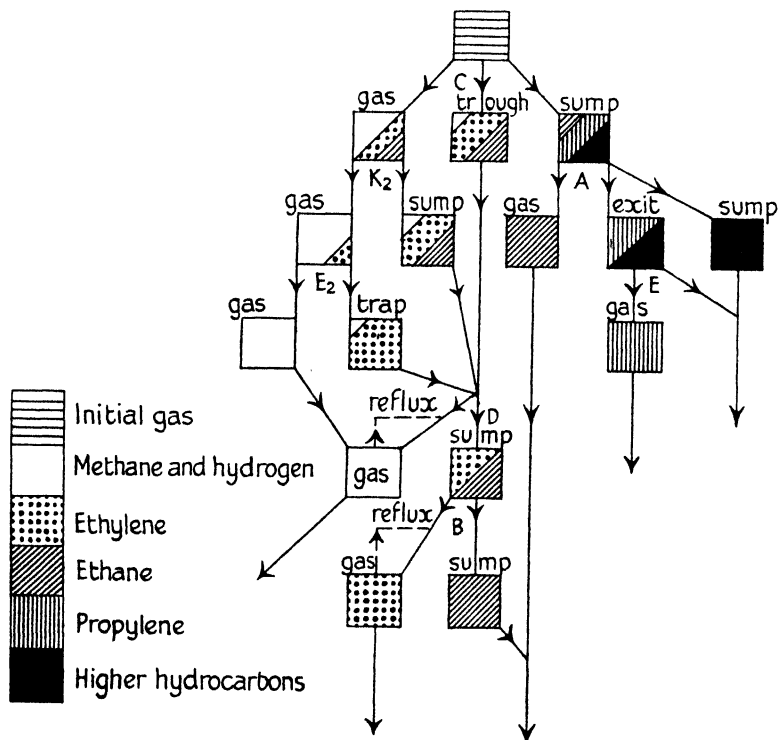


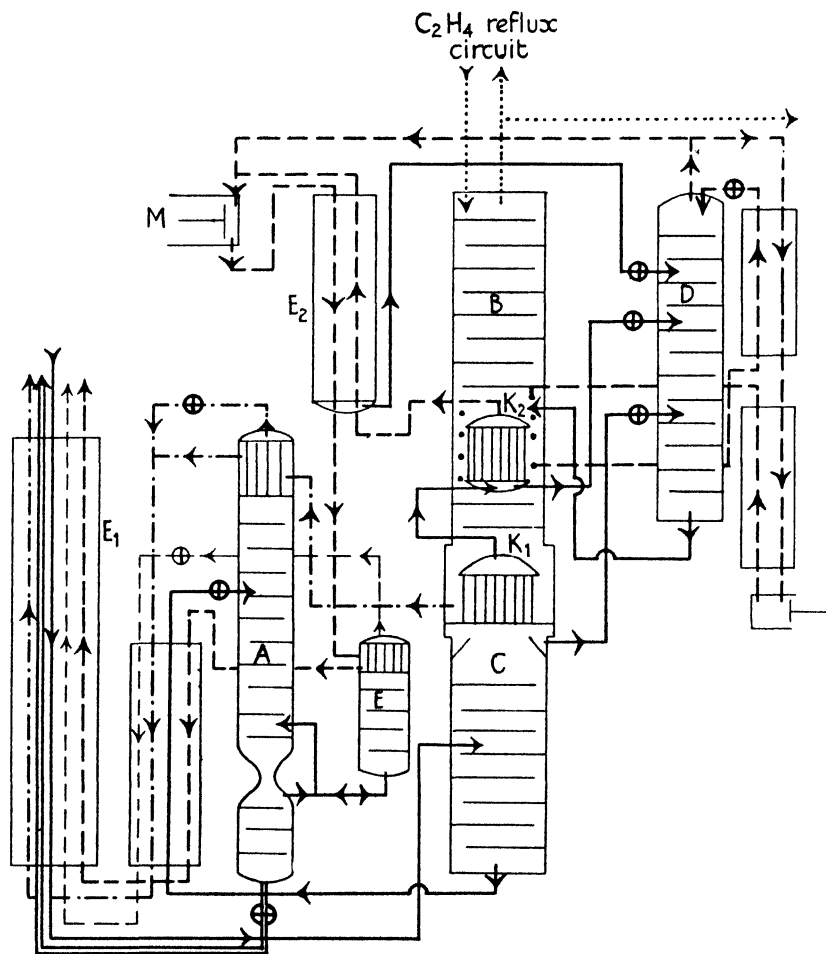
FIG. 147. Diagram showing stages of separation in American cracker-gas plant

and a condenser  $K_1$ . One liquid fraction collects in the sump, the other in a trough under the condenser. All the ethylene is contained in the latter fraction and the effluent; all the propylene in the sump. The effluent is freed of ethylene in the condenser  $K_2$  and finally in an exchanger  $E_2$ , in which it is cooled by the methane-hydrogen mixture which has traversed the expansion engine  $M$ .

At this stage the following phases have been separated:

- a liquid fraction containing all the propylene and no ethylene;
- a gas containing neither ethylene nor propylene;
- three liquid fractions containing together all the ethylene and no propylene (one in the trough of  $C$ , one in the sump of  $K_2$ , and one in a trap under  $E_2$ ).

These three fractions are thereupon united in the auxiliary column *D*, provided with a reflux of liquid methane, and are thus separated into a liquid fraction containing only ethylene and ethane and an



— Cracker gas and intermediate fractions — Methane and hydrogen  
 ..... Ethylene --- Ethane ---- Propylene == Heavy fraction

FIG. 148. American plant for separating cracker gas

effluent containing only methane and hydrogen. This gas is united with the effluent from  $K_2$ , and we now have

- a liquid containing all the propylene and no ethylene;
- a gas containing neither ethylene nor propylene;
- a liquid containing all the ethylene and some ethane.

This last liquid is rectified in the column *B* above *C*, where it is provided with a reflux of liquid ethylene. It results in the final separation of all the ethylene. The methane and ethylene refluxes are obtained by recompression and cooling of the products. In this way the original effluent and the liquid formed in the trough of *C* have been separated into three parts:

- (1) hydrogen and methane;
- (2) ethylene;
- (3) ethane.

The propylene fraction is separated in the auxiliary columns *A* and *E* into the following corresponding parts:

- (1) ethane;
- (2) propylene;
- (3) propane, butylenes, etc.

It is unnecessary to go into further detail in discussing the plant, as it is described in the patent specification merely as an example and is obviously capable of a number of variations. It is exceedingly complicated and it appears doubtful whether it is indeed an improvement on the apparatus described first. The use of expansion engines and compressors offers few advantages over the independent ethylene and ammonia cycles, as they render the whole plant less elastic. Small adjustments can be made more easily if independent cycles are used. The examples given should, however, offer a fair survey of the manifold ways of applying well-known separating units to complicated mixtures of the type of cracker gas.

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